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(DOKLADY AKADEMII NAUK SSSR)

Chemistry Section

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NITRATION OF SOME α,β-UNSATURATED ALDEHYDES AND KETONES OF THE FURAN SERIES

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In our earlier communications, we reported the results of an investigation of the condensation of 5-nitrofurfural with acetaldehyde [1] and the nitration of monofurfurylidenacetone (I) [2].

The second of these two methods for the preparation of nitrofurans has a number of advantages over the condensation of 5-nitrofurfural and its derivatives with carbonyl-containing compounds. Therefore, it was of definite interest to investigate the possibility of synthesizing substituted α,β-unsaturated aldehydes and ketones of the 5-nitrofuran series by nitration of the corresponding furan compounds.

Despite individual attempts to carry out syntheses by this route, such syntheses have not been successful up to the present time. Thus, Sasaki [3] reported unsuccessful attempts to nitrate β-(2-furyl)acrylaldehyde (II) and monofurfurylidenacetone (I), and Saikachi and co-workers [4] obtained only tarry condensation products of the starting materials when they attempted to nitrate α-methyl-β-(2-furyl)acrylaldehyde (III) with acetyl nitrate.

We have been able to carry out successfully the nitration of β-(2-furyl)acrylaldehyde (II) and certain of its α-alkyl (III-VI) and α-alkoxymethyl (VII and VIII) derivatives (see Table 1) by using conditions different from those employed by the earlier authors. These differences were, first, a lower reaction temperature (from −25 to −30°) and , second, the use of small additions of concentrated sulfuric acid as a catalyst. The presence of H_2SO_4 apparently sufficiently increases the concentration and the rate of formation of nitronium ions (NO_2^+) in the acetic anhydride solution [5-9] that the nitration reaction predominates over the side reactions.

Table 1 shows the yields and properties of the α,β-unsaturated aldehydes of the nitrofuran series (X-XXIII) synthesized by this new route.

The following mechanism may be proposed for the nitration of α,β-unsaturated aldehydes of the furan series:

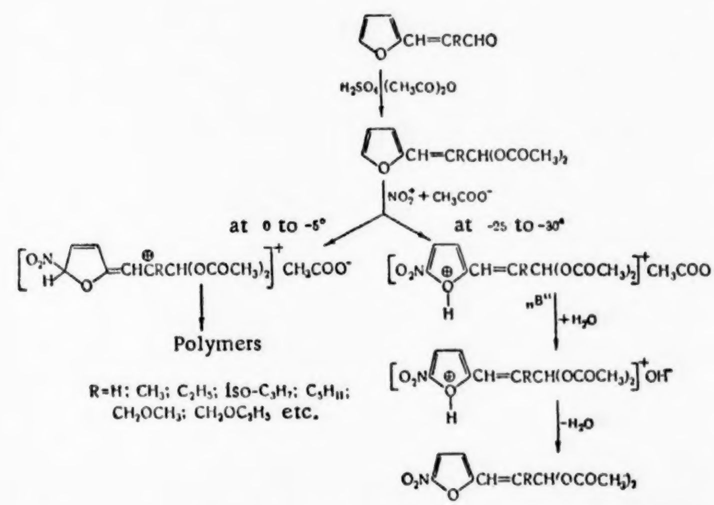

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TABLE 1. Nitration Products and Their Derivatives

Initial compound HC=CH–CH=C–CH=C–CO–R_2 (ring –O–; R_1)		Structural formula of product ($Y=O_2N$–C=CH–CH=C–CH=C–; ring –O–; R_4)		M. p., °C	Yield, %	C, %		H, %		N, %		Ultraviolet absorption spectrum ($\epsilon \cdot 10^{-3}$)
						found	calcd.	found	calcd.	found	calcd.	
R_1=H; R_2=H	(II)	YCH $(OCOCH_3)_2$	(X)	97–98	25–30*	48,93	49,03	4,17	4,12	5,22	5,20	342 (13,00); 222 (13,10)
		YCHO	(XI)	117–118	90	50,48	50,31	3,10	3,02	8,45	8,38	343 (16,20); 237 (11,80)
		YCH=$NNHCONH_2$	(XII)	242 (dec.)	92	—	—	—	—	25,01	24,99	392 (23,90); 292 (22,80)
$R_1=CH_3$; R_2=H	(III)	YCH $(OCOCH_3)_2$	(XIII)	113–114	42*	50,81	50,87	4,45	4,63	5,21	4,95	350 (16,86); 231 (19,60)
		YCHO	(XIV)	94,5–95,5	94	53,23	53,04	4,10	3,90	7,69	7,73	347 (24,40); 284 (8,30); 244 (22,66)
		YCO=$NNHCONH_2$	(XV)	240 разл.	93	45,46	45,38	4,37	4,23	23,31	23,52	395 (24,00); 292 (19,60)
$R_1=C_2H_5$; R_2=H	(IV)	YCH $(OCOCH_3)_2$	(XVI)	100–101	21*	52,70	52,52	4,93	5,09	4,97	5,71	350 (16,50); 232 (18,80)
		YCHO	(XVII)	74–75	92	55,51	55,38	4,57	4,65	7,38	7,18	350 (16,50); 285 (5,80); 245 (9,20)
		YCH=$NNHCONH_2$	(XVIII)	219–220 (dec.)	91	—	—	—	—	22,21	22,56	
R_1 iso-C_3H_7; R_2=H	(V)	YCH=$NNHCONH_2$	(XIX)	214 (dec.)	17*	49,40	49,62	5,32	5,30	21,43	21,04	390 (16,70); 292 (16,20) 224 (9,56)
$R_1=C_5H_{11}$; R_2=H	(VI)	YCH=$NNHCOCH_2CN$	(XX)	162–163	37*	—	—	—	—	17,96	17,60	385 (24,00); 284 (29,40)
$R_1=CH_2OCH_3$; R_2=H	(VII)	YCHO	(XXI)	118–119	17*	51,54	51,19	4,36	4,30	6,50	6,63	345 (14,10); 243 (7,80)
		YCH=$NNHCONH_2$	(XXII)	222–223 (dec.)	95	44,89	44,78	4,60	4,51	21,24	20,89	393 (21,40); 292 (18,70)
$R_1=CH_2OC_2H_5$; R_2=H	(VIII)	YCH=$NNHCONH_2$	(XXIII)	219–220 (dec.)	17*	—	—	—	—	19,62	12,85	388 (20,60); 293 (20,00); 247 (10,04); 224 (11,72)
R_1=H; $R_2=C(CH_3)_3$	(IX)	YCOC $(CH_3)_3$	(XXIV)	108–109	34*	59,10	59,19	5,80	5,87	6,33	6,28	347 (21,10); 243 (12,00)

* Yield in the nitration stage.

The initial fundamental act is evidently the formation of oxonium cation B, which exists in the acetic anhydride solution.

When, after nitration was complete, the reaction mixture was poured into ice water, an oily intermediate product initially separated, and this was converted into the final, solid product when the mixture was further stirred with water.

TABLE 2

Compound*		M. p., °C	N, %	
			found	calcd.
$RCH{=}C(CH_3)CH{=}NNHCO{-}C_5H_4N$ **	(XXV)	236–7 (dec.)	19.02	18.66
$RCH{=}C(CH_3)CH{=}NNHCOCH_2CN$	(XXVI)	243–4 (dec.)	21.54	21.37
$RCH{=}C(CH_3)CH{=}NZ$	(XXVII)	244–6 (dec.)	15.55	15.84
$RCH{=}C(C_2H_5)CH{=}NNHCOCH_2CN$	(XXVIII)	219 (dec.)	20.40	20.28
$RCH{=}C(C_2H_5)CH{=}NZ$	(XXIX)	220–221 (dec.)	15.01	15.05
$RCH{=}C(iso\text{-}C_3H_7)CH{=}NNHCSNH_2$	(XXX)	185–4 (dec.)	19.66	19.85
$RCH{=}C(iso\text{-}C_3H_7)CH{=}NNHCOCH_2CN$	(XXXI)	185–6 (dec.)	18.94	19.30
$RCH{=}C(iso\text{-}C_3H_7)CH{=}NX$	(XXXII)	229–230 (dec.)	18.29	18.29
$RCH{=}C(C_5H_{11})CH{=}NNH{-}C_6H_3(NO_2){-}NO_2$	(XXXIII)	159–160	16.84	16.78
$RCH{=}C(CH_2OCH_3)CH{=}NNHCSNH_2$	(XXXIV)	186 (dec.)	19.66	19.71
$RCH{=}C(CH_2OCH_3)CH{=}NNHCO{-}C_5H_4N$ **	(XXXV)	190 (dec.)	17.18	16.96
$RCH{=}C(CH_2OCH_3)CH{=}NNHCOCH_2CN$	(XXXVI)	188 (dec.)	18.89	19.17
$RCH{=}C(CH_2OCH_3)CH{=}NOH$	(XXXVII)	139–140	12.48	12.39
$RCH{=}C(CH_2OCH_3)CH{=}NX$	(XXXVIII)	dec. >250	17.90	18.18
$RCH{=}C(CH_2OCH_3)CH{=}NZ$	(XXXIX)	175–7 (dec.)	14.29	14.24
$RCH{=}C(CH_2OC_2H_5)CH{=}NNHCOCH_2CN$	(XL)	192–4 (dec.)	18.33	18.30
$RCH{=}C(CH_2OC_2H_5)CH{=}NX$	(XLI)	232–5 (dec.)	17.11	17.39
$RCH{=}C(CH_2OC_2H_5)CH{=}NZ$	(XLII)	176–7 (dec.)	13.50	13.59
$RCH{=}CHC(CH_3){=}NNHCSNH_2$	(XLIII)	210 (dec.)	22.20	22.04
$RCH{=}CHC(CH_3){=}NNHCOCH_2CN$	(XLIV)	225 (dec.)	21.53	21.37
$RCH{=}CHC(CH_3){=}NOH$	(XLV)	175–7 (dec.)	14.43	14.28
$RCH{=}CHC(CH_3){=}NNHCO{-}C_5H_4N$ **	(XLVI)	225 (dec.)	18.74	18.66
$RCH{=}CHC(CH_3){=}NNHCOR$	(XLVII)	235–6 (dec.)	16.62	16.77
$RCH{=}CHC(CH_3){=}NNHCO{-}\underbrace{C{=}CH{-}CH{=}CBr}_{O}$	(XLVIII)	215–7 (dec.)	11.75	11.42
$RCH{=}CHC(CH_3){=}N{-}N{=}C(CH_3)CH{=}CHR$	(XLIX)	188–9	15.65	15.64
$RCH{=}CHC(CH_3){=}NN(CH_2CH_2OH)COCONH_2$	(L)	181–5 (dec.)	18.11	18.06
$RCH{=}CHC(CH_3){=}NNH{-}C_6H_3(NO_2){-}NO_2$	(LI)	257 (dec.)	19.06	19.38

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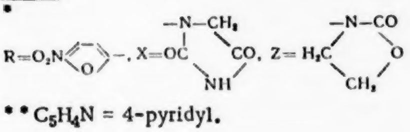

** C_5H_4N = 4-pyridyl.

It is known that, in accordance with the viewpoints of Freure and Johnson [10], Clauson-Kaas and Fakstorp [11] and others [12, 13], a similar intermediate product is formed during the nitration of acidophobic furans, and these intermediates have been assigned the structure of 2-acetoxy-5-nitro-2,5-dihydrofurans (A). The latter readily splits out acetic acid under the influence of basic reagents. However, a structure such as A cannot explain the ease with which the so-called "intermediate" product in our case is converted to the final nitro compound by the action of water only.

The structure of the oily intermediate products formed during nitration of α, β-unsaturated aldehydes II-VIII of Table 1 is apparently better described by the oxonium structure $B^+CH_3COO^-$ of the mechanism presented above. Thus, again in the present case it has been possible to show the presence of low-stability intermediate oxonium compounds during the nitration of acidophobic furans. One of the present authors has previously expressed certain opinions on this subject [5, 6].

In conclusion, it should be pointed out that we were unable successfully to carry out by this route the nitration of aldehydes and ketones of the furan series containing two or more conjugated double bonds in the side chain, for example, 5-(2-furyl)-2,4-pentadienal, 1-(2-furyl)-1,3-hexadien-5-one, 1,5-bis(2-furyl)-1,4-pentadien-3-one, and 1,9-bis(2-furyl)-1,3,6,8-nonatetraen-5-one.

On the other hand, nitration of 4,4-dimethyl-1-(2-furyl)-1-penten-3-one proceeded comparatively smoothly; this represents the first time this reaction has been carried out successfully (see Table 1, IX).

Table 2 presents information on the numerous derivatives of α, β-unsaturated nitrofuran aldehydes and ketones in which the derivative was formed at the carbonyl group (XXV-LI).

The antibacterial, antituberculosis, and fungistatic properties of these compounds will be described in detail in one of our forthcoming communications.

EXPERIMENTAL

Nitration of α, β-unsaturated aldehydes (see Table 1). The nitration mixture, which was prepared from 266 g of acetic anhydride, 9.4 g of purified nitric acid [14] (sp. gr. 1.51), and 0.5 g of sulfuric acid (sp. gr. 1.84), was cooled to −30°, and a solution of 0.1 mole of the (2-furyl)-alkenal (II-VIII) in 40 ml of acetic anhydride was added dropwise and with stirring; the addition was carried out over a period of an hour. The nitration product was separated by pouring the reaction mixture into 500 g of ice in 500 ml of water and stirring for 3-4 hr. The final crystalline diacetates of α, β-unsaturated 5-(nitro-2-furyl)alkenals X, XIII, and XVI were purified by recrystallization from alcohol or tetrahydrofuran. Conversion of diacetates X, XIII, and XVI to the corresponding aldehydes XI, XIV, and XVII was accomplished by heating with 20% H_2SO_4 at 90-95° for 10 minutes.

In the nitration of α, β-unsaturated furan aldehydes V-VIII, the corresponding final nitro products could not be separated as crystalline compounds. In the case of VII, hydrolysis of the diacetate with 20% H_2SO_4 at 90-95° for 10 min gave the crystalline aldehyde XXI, while in the case of the other starting materials, the corresponding hydrazones XIX, XX, XXII, and XXIII were prepared. The structures of these hydrazones were proved by elemental analysis and by ultraviolet absorption spectroscopy. The absorption maxima of these compounds were in complete agreement with those of similar derivatives of known α, β-unsaturated 5-(nitro-2-furyl)alkenals [6].

Nitration of 4,4-dimethyl-1-(2-furyl)-1-penten-3-one (XI) was carried out by the method previously described by us for the nitration of monofurfurylidenacetone (I) [2].

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CONTRIBUTION TO THE PROBLEM OF THE STABILITY OF COMPLEX COMPOUNDS OF DIVALENT PLATINUM

COMPOUNDS OF THE TETRAAMINE TYPE

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Compounds of the tetraamine type containing the complex ion $[PtA_4]^{2+}$, where A is an ammonia or amine molecule, have received considerable study. However, there is no information in the literature relative to the thermodynamic stability of these complex ions. It is known from preparative data that the ammonia molecule, as well as aliphatic amine molecules, have a greater tendency toward complex formation with divalent platinum ions than do Cl^-, Br^-, and I^-.

Certain conclusions may be formed on the basis of the literature as regards the relative stability of ammonia and amine complexes. In a study of equilibria of the type

$$\text{trans-}[C_2H_4H_2OPtCl_2] + A \rightleftarrows \text{trans-}[C_2H_4APtCl_2] + H_2O,$$

Chatt and Gamlen [1] found log K = 7.8 in the case in which A = NH_3, while for A = CH_3NH_2, log K = 8.6. Hence, it follows that the methylamine molecule is held more tightly in the inner sphere than is the ammonia molecule.

A study of the acid properties of complexes of tetravalent platinum with ammonia and aliphatic amines [2] revealed that the acid dissociation constant of newly synthesized $[Pt(CH_3NH_2)_4NH_3Cl]^{3+}$ is $K_1 = 1.7 \cdot 10^{-7}$, while the corresponding value for the ion $[Pt(NH_3)_5Cl]^{3+}$ under the same conditions is $6.4 \cdot 10^{-9}$. Therefore, it may be concluded that a methylamine molecule coordinated in the inner sphere of Pt^{IV} will be deformed to a greater extent than will a molecule of ammonia.

The present work was devoted to a determination of the over-all instability constants of $[PtA_4]^{2+}$ ions containing an ammonia, methylamine, ethylamine, or ethylenediamine molecule in the inner sphere.

EXPERIMENTAL

The determination of the overall instability constants of complex tetraamines of divalent platinum was carried out by the potentiometric method previously used by us in an investigation of platinites [3]. E.m.f. measurements were carried out for the cell

$$\overset{+}{Pt} \mid \underset{c_1}{[PtA_4]Cl_2},\ \underset{c_2}{A},\ KNO_3 \parallel \underset{\text{sat.}}{KCl},\ Hg_2Cl_2 \mid \overset{-}{Hg}$$

at different concentrations of complexes and ligands.

The measurements were carried out by the usual compensation method with a PRTV-49 potentiometer and an indicating galvanometer. The cell containing a platinized platinum electrode and a saturated calomel electrode was placed in a thermostatted bath at a temperature of 18 ± 0.5°. The platinum electrodes were prepared from platinum plate, 20 x 10 mm, covered with electrolytically deposited platinum black.

The actual carrying out of the measurements was as follows: Ten ml of a solution of a specific concentration of ammonia or the appropriate amine was introduced into a special cell. A weighed amount of the complex was introduced into the solution, and, finally, KNO_3 was added in the amount required to maintain the solution at a constant ionic strength of unity. The electrodes and the salt bridge, which was filled with a 1 N solution of KNO_3, were then immersed in the solution. The cell was placed in the thermostatted bath, and the

solution was saturated with nitrogen. Measurements were made from the moment the salt dissolved to the time when a practically constant value of the potential was established.

The substances investigated were synthesized as follows:

Tetraaminoplatinum dichloride $[Pt(NH_3)_4]Cl_2$. Peyronet's salt was prepared from potassium chloroplatinite [4]. Solution of this in excess ammonia and subsequent crystallization gave the required tetraamine. For purposes of comparison, experiments were also carried out with tetraamine prepared directly from the platinite by the method of Gil'dengershel' [5].

Tetra(methylamino)platinum dichloride $[Pt(CH_3NH_2)_4]Cl_2$. Cis-di(methylamino)platinum diiodide was synthesized from platinum chloroplatinite, and this was converted to cis-di(methylamino)platinum dichloride [6], solution of which in excess methylamine gave a solution of the tetraamine. The solution was concentrated to a syrup, and cooling of the solution yielded crystals of tetra(methylamino)platinum dichloride.

Tetra(ethylamino)platinum dichloride $[Pt(C_2H_5NH_2)_4]Cl_2$. The calculated amount of a solution of ethylamine was added to a chloroplatinite solution. On the following day, the same amount of ethylamine was added to the solution, in which a precipitate had formed. The solution was stirred continuously on a boiling water bath, and the precipitate dissolved. The solution was concentrated and cooled, and the tetra(ethylamino)platinum dichloride was precipitated with alcohol [5].

Di(ethylenediamine)platinum dichloride $[Pt(NH_2C_2H_4NH_2)_2]Cl_2$ was synthesized in a manner similar to that used for tetra(ethylamino)platinum dichloride. The composition of all four substances was established by chemical analysis.

The ammonia and the amines were purified by distillation. All solutions were prepared with doubly distilled water.

The experimental data obtained with the amine and the tetraamines are presented in Tables 1-4.

The concentration of Pt^{2+} ions was calculated from the measured electrode potentials (assuming the standard Pt/Pt^{2+} potential to be 1.2 v), and the value of the overall instability constant was then calculated by means of the formula:

$$K^c = \frac{[Pt^{2+}]\cdot[A]^4}{[PtA_4^{2+}]} \qquad \text{for } A = NH_3,\ CH_3NH_2,\ C_2H_5NH_2;$$

$$K^c = \frac{[Pt^{2+}]\,[C_2H_4(NH_2)_2]^2}{[Pt(NH_2CH_2CH_2NH_2)_2^{2+}]} \qquad \text{for } A = C_2H_4(NH_2)_2.$$

TABLE 1. Determination of the Instability Constant of $[Pt(NH_3)_4]^{2+}$

Expt. No.	Conc. of $[Pt(NH_3)_4]Cl_2$ mole/liter	Conc. of NH_3, mole/liter	$E = E_{Pt} - E_{cal}$ mv	E_{Pt}, mv	$-\lg[Pt^{2+}]$	pK^c
1	0,0029	$0,92\cdot10^{-1}$	2	250	32,8	34,5
2	0,0429	$0,92\cdot10^{-1}$	23	271	32,1	34,9
3	0,0024	$4,2\cdot10^{-2}$	28	276	31,9	34,7
4	0,0352	$4,2\cdot10^{-2}$	46	294	31,3	35,4
5	0,0077	$4,2\cdot10^{-3}$	124	372	28,6	36,0
6	0,0418	$4,2\cdot10^{-3}$	170	418	27,0	35,1
7	0,0023	$4,2\cdot10^{-4}$	246	494	24,4	35,3
8	0,0085	$6,9\cdot10^{-4}$	240	488	24,6	35,2
9	0,0356	$6,9\cdot10^{-4}$	227	475	25,0	36,2
10	0,0051	$1,2\cdot10^{-5}$	403	651	18,9	35,5
11	0,0012	$1,2\cdot10^{-5}$	408	656	18,8	36,2

Average pK^c = 35.3.

In addition to solutions of the free bases, a 1 N solution of ammonium nitrate (in the case of $[Pt(NH_3)_4]Cl_2$) and a 1 N solution of methylamine hydrochloride (in the case of $[Pt(CH_3NH_2)_4]Cl_2$) were used. The concentrations of NH_3 and CH_3NH_2 were calculated on the basis of the hydrolysis constants of the salts and pH data measured in the the solutions investigated. The experimental data and the calculations of the instability constants of these solutions are shown as experiments Nos. 10 and 11 (Table 1) and 8-10 (Table 2).

DISCUSSION

The data presented in Tables 1 to 4 show that with a change in the concentration of the complex and a change in the concentration of the ligand (by a factor of 1000 to 10,000), the values of the concentration instability constants remained constant within one-and-a-half units.

TABLE 2. Determination of the Instability Constant of $[Pt(CH_3NH_2)_4]^{2+}$

Expt. No.	Conc. of $[Pt(CH_3NH_2)_4]Cl_2$ mole/liter	Conc. of CH_3NH_2, mole per liter	$E = E_{Pt} - E_{cal}$, mv	E_{Pt}, mv	$-\lg[Pt^{2+}]$	pK^c
1	0,002	$1,45 \cdot 10^{-2}$	—45	203	34,4	39,1
2	0,0361	$1,45 \cdot 10^{-2}$	—41	207	34,2	40,1
3	0,0022	$1,58 \cdot 10^{-3}$	15	263	32,3	40,8
4	0,0337	$1,58 \cdot 10^{-3}$	66	314	30,6	40,3
5	0,0026	$1,45 \cdot 10^{-4}$	186	434	26,4	39,4
6	0,0384	$1,45 \cdot 10^{-4}$	215	463	25,4	39,3
7	0,0291	$1,45 \cdot 10^{-5}$	282	530	23,1	40,9
8	0,0021	$2,3 \cdot 10^{-6}$	348	596	20,8	40,5
9	0,001	$1,55 \cdot 10^{-6}$	374	622	19,9	40,1
10	0,0083	$3,46 \cdot 10^{-6}$	338	586	21,2	40,7

Average $pK^c = 40.1$.

TABLE 3. Determination of the Instability Constant of $[Pt(C_2H_5NH_2)_4]^{2+}$

Expt. No.	Conc. of $[Pt(C_2H_5NH_2)_4]Cl_2$ mole/liter	Conc. of $C_2H_5NH_2$ mole per liter	$E = E_{Pt} - E_{cal}$, mv	E_{Pt}, mv	$-\lg[Pt^{2+}]$	pK^c
1	0,0019	$3,8 \cdot 10^{-2}$	—45	203	34,4	37,4
2	0,0154	$3,8 \cdot 10^{-2}$	—19	229	33,5	37,3
3	0,059	$3,8 \cdot 10^{-2}$	7	255	32,6	37,1
4	0,0036	$3,9 \cdot 10^{-3}$	85	333	29,9	37,1
5	0,0123	$3,9 \cdot 10^{-3}$	121	369	28,7	36,4
6	0,0608	$3,9 \cdot 10^{-3}$	110	358	29,0	37,4
7	0,0054	$3,9 \cdot 10^{-4}$	222	470	25,2	36,6
8	0,0036	$3,9 \cdot 10^{-5}$	332	580	21,4	36,6
9	0,0216	$3,9 \cdot 10^{-5}$	340	588	21,1	37,1

Average $pK^c = 37.0$.

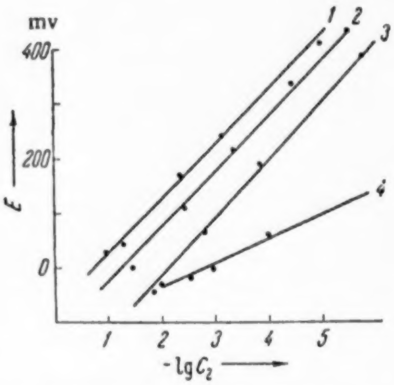
TABLE 4. Determination of the Instability Constant of $[Pt(NH_2C_2H_4NH_2)_2]^{2+}$

Expt. No.	Conc. of $[Pt(NH_2C_2H_4NH_2)_2]Cl_2$ mole/liter	Conc. of $C_2H_4(NH_2)_2$ mole/liter	$E = E_{Pt} - E_{cal}$, mv	E_{Pt}, mv	$-\lg[Pt^{2+}]$	pK^c
1	0,003	$1,11 \cdot 10^{-2}$	—54	194	34,7	36,1
2	0,0442	$1,11 \cdot 10^{-2}$	—22	226	33,6	36,2
3	0,0025	$1,11 \cdot 10^{-3}$	—1	247	32,9	36,2
4	0,0547	$1,11 \cdot 10^{-3}$	+9	257	32,5	37,1
5	0,003	$3,14 \cdot 10^{-3}$	—45	203	34,4	36,9
6	0,0307	$3,14 \cdot 10^{-3}$	—25	223	33,7	36,2
7	0,0035	$1,0 \cdot 10^{-4}$	71	319	30,4	36,0
8	0,0262	$1,0 \cdot 10^{-4}$	58	306	30,8	37,2

Average $pK^c = 36.5$.

A comparison of the stability of the ethylenediamine complex with that of the other tetraamines on the basis of the instability constants is not entirely correct, since the equation used to calculate the constant for the first complex contains the square of the molar concentration of the ligand, while the equation used for the remaining complexes contains the concentration to the fourth power. It is more correct to compare the concentrations of the

Pt^{2+} ions for the various complexes at constant concentrations of complexes and ligands. A graph showing the variation in e.m.f. values with log C_A (Fig. 1) was constructed for this purpose. The figure shows that of the amines studied, ethylenediamine forms the most stable complex.



Dependence of electrode potential on ligand concentration at a constant complex concentration of C_1 = 0.04 mole/liter. 1) $[Pt(NH_3)_4]^{2+}$; 2) $[Pt(C_2H_5NH_2)_4]^{2+}$; 3) $[Pt(CH_3NH_2)_4]^{2+}$; 4) $[Pt(NH_2CH_2CH_2NH_2)_2]^{2+}$.

It is interesting to compare the data presented in the present paper with those previously published for platinites. Such a comparison leads to the following series of increasing thermodynamic stability:

$$\begin{array}{lccccc} & [PtCl_4]^{2-} < & [PtBr_4]^{2-} < & [PtI_4]^{2-} < & [Pt(NH_3)_4]^{2+} < & [Pt(C_2H_5NH_2)_4]^{2+} \\ pK & 16.6 & 20,4 & 29,6 & 35,3 & 37,0 \end{array}$$

$$\begin{array}{ccc} < [Pt(CH_3NH_2)_4]^{2+} < & Pt(CN)_4]^{2-} < & [Pt(NH_2C_2H_4NH_2)_2]^{2+} \\ 40,1 & 41,0 & \end{array}$$

It should be noted that these complex ions of the tetraamine type are characterized simultaneously both by a considerable thermodynamic stability and by a high inertness in the sense of Taube. At the same time, the thermodynamically very stable ion $[Pt(CH)_4]^{2-}$ is also very reactive. The inertness of tetraamine complexes is apparently associated with the small trans influence of the ammonia and amine molecules in the inner sphere of divalent platinum.

It is interesting that this inertness did not hinder relatively rapid establishment of the potential at the platinum electrode. It may be assumed that processes of the following type occur in these systems:

$$Pt^0 + Pt^{2+}(NH_3)_4]^{2+} \rightarrow Pt^{2+} + [Pt^0(NH_3)_4]^0 \rightarrow Pt^0 + 4NH_3$$
$$Pt^{2+} + 4NH_3 \rightarrow [Pt^{2+}(NH_3)_4]^{2+},$$

i.e., there is an exchange of platinum between the complex ions and the electrode.

It is understood that the values of the instability constants obtained in the present work are provisional in the sense that they were calculated using a value of 1.2 v for the potential of $Pt^{2+} + 2e \rightarrow Pt$. However, if this value is determined more accurately at some future date, the introduction of the appropriate correction will not be reflected in the stability series of complex ions presented above.

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ON THE SEPARATION OF ASYMMETRIC ARSONIUM COMPOUNDS INTO THE OPTICALLY ACTIVE ANTIPODES

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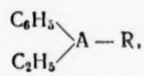
At the present time there is only a very small number of papers devoted to the separation of quaternary salts of asymmetric arsonium compounds of the general type RR'R"R'"AsHAL, in which optical activity undoubtedly depends on the arsenic atom.

After unsuccessful attempts in this direction by Michaelis [1] and by Winmill [2], in 1921 Burrows and Turner [3] separated the dextrorotatory form of methylphenylbenzyl-α-naphthylarsonium iodide, $M_D = 12°$, which changed to the inactive form upon recrystallization. Somewhat later, one of us was able to separate the dextrorotatory form of ethyl-n-propyl-p-tolylbenzylarsoniumiodide, $M_D = 41.5°$, by decomposition of ethyl-n-propyl-p-tolylbenzylarsonium D-π-bromocamphorsulfonate with an aqueous solution of potassium iodide.

Continuing our investigations in this field, we have synthesized various asymmetric arsines of the general formula:



where R is an aliphatic radical, by the interaction of phenylethylchloroarsine with organomagnesium compounds of the corresponding alkyl halides. Some physical constants of these arsines are shown in Table 1.

TABLE 1

Compound	B. p., °C at 10 mm	d_4^{20}	n_D^{20}	As, %	
				calcd.	found
$(C_6H_5)(C_2H_5)(CH_3) \equiv As$	85—86	1,2023	1,5642	38,21	37,98
$(C_6H_5)(C_2H_5)(C_3H_7) \equiv As$	108—109	1,1415	1,5492	33,45	33,28
$(C_6H_5)(C_2H_5)(C_4H_9) \equiv As$	122—123	1,1187	1,5438	31,45	31,27
$(C_6H_5)(C_2H_5)(C_5H_{11}) \equiv As$	133—134	1,0971	1,5371	29,70	29,59
$(C_6H_5)(C_2H_5)(C_6H_{13}) \equiv As$	145—146	1,0862	1,5340	28,20	27,90
$(C_6H_5)(C_2H_5)(C_7H_{15}) \equiv As$	163—164	1,0661	1,5271	26,72	26,53
$(C_6H_5)(C_2H_5)(C_8H_{17}) \equiv As$	171—172	1,0514	1,5221	25,45	25,28
$(C_6H_5)(C_2H_5)(C_9H_{19}) \equiv As$	181—182	1,0327	1,5170	24,29	24,23

These tertiary asymmetric arsines are colorless liquids (with an unpleasant odor) which are readily miscible with alcohol, ether, benzene, and other organic solvents.

Further, by the addition of allyl bromide or benzyl bromide to certain of these arsines, we were able to prepare the corresponding asymmetric quaternary arsonium compounds in the crystalline state; some data on these compounds are presented in Table 2.

These asymmetric arsonium compounds were white crystalline substances which were soluble in alcohol, acetone, and water and insoluble in ether. They were hygroscopic. The allyl derivatives were more hygroscopic than the benzyl compounds. The introduction of a benzyl radical into a quaternary arsonium compound makes the latter more sensitive to air.

Re-solution of the asymmetric arsonium compounds was carried out by means of the optically active silver salt of D-π-bromocamphorsulfonic acid. When the arsonium salts were reacted with the silver D-π-bromocamphorsulfonate only ethyl-n-amylphenylbenzylarsonium D-π-bromocamphorsulfonate crystallized readily. The remaining salts formed syrups.

TABLE 2

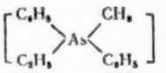
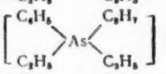
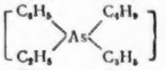
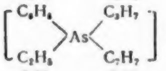
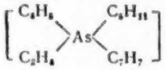
Compound	M. p., °C at 10 mm	As, % calcd.	As, % found	Br, % calcd.	Br, % found	Yield, %
 Br	84—85	23,30	23,62	25,10	25,10	93,1
 Br	105—106	21,75	21,74	23,06	23,15	93,9
 Br	77—78	20,95	21,14	22,35	22,25	87,8
 Br	154,156	18,95	18,78	20,22	20,33	84,7
 Br	108—109	17,69	17,60	18,88	18,94	79,2

TABLE 3

Fraction No.	Amount, g	Amt. of solvent, g	α_D	$[\alpha]_D$	$[M]_\alpha$	Difference, ΔM
1	0,0441	2	+0,35	+53,2	+347,7	+74,7
2	0,1491	2	+1,20	+53,4	+348,3	+75,3
3	0,0187	2	−0,10	−34,2	−222,3	−51,1

The experiment on the separation of ethyl-n-amylphenylbenzylarsonium bromide by means of silver D-π-bromocamphorsulfonate was carried out as follows.

An aqueous solution of 8.01 g of ethyl-n-amylphenylbenzylarsonium bromide was poured into a solution of 7.91 g of the silver salt of D-π-bromocamphorsulfonic acid. After the precipitated silver bromide had been separated by filtration, the water was distilled under vacuum. The ethyl-n-amylphenylbenzylarsonium D-π-bromocamphorsulfonate, which remained in the distillation flask, crystallized. The contents of the flask were then dissolved in ethyl acetate. After distillation of a part of the solvent and prolonged standing of the residue, a first fraction of crystals separated as needles, and then, after evaporation of part of the remaining solvent and further standing of the residue, a second fraction of crystals separated. The m. p. of the crystals of the first fraction was 159°. Found %: As 11.50; calculated for $C_{30}H_{42}O_4SBrAs$. Calculated %: As 11.46.

The m. p. of the crystals of the second fraction was 156°. Found %: As 11.48; calculated for $C_{30}H_{42}O_4SBrAs$. Calculated %: As 11.46.

Crystals were also separated from the remaining mother liquor. Found %: As 11.39; calculated for $C_{30}H_{42}O_4SBrAs$ 11.46.

The results of polarimetric measurements are shown in Table 3. The measurements were carried out in a 3-centimeter tube.

Further, with the aim of obtaining the optical isomers in the pure form, the diastereoisomers were decomposed with an aqueous solution of potassium bromide. However, only decomposition of the diastereoisomers of the first fraction of crystals led to the desired results; crystals with an m. p. of 111° were obtained. Found %: As 16.99; calculated for $C_{20}H_{28}AsBr$. Calculated %: As 17.69.

Polarimetric measurements gave: $\alpha_D = +0.10°$; $[\alpha]_D = +16.5°$; $[M]_D = +70.0°$.

This dextrorotatory component rapidly changed to the inactive form.

Thus, the dextro- and levorotatory diastereoisomers were obtained:

$$d\left[\begin{array}{c}C_6H_5\\C_2H_5\end{array}\!\!>As<\!\!\begin{array}{c}C_5H_{11}\\C_7H_7\end{array}\right]\text{-}d\text{-}\pi\text{-}C_{10}H_{14}OBrSO_3;$$

$$l\left[\begin{array}{c}C_6H_5\\C_2H_5\end{array}\!\!>As<\!\!\begin{array}{c}C_5H_{11}\\C_7H_7\end{array}\right]\text{-}d\text{-}\pi\text{-}C_{10}H_{14}OBrSO_3$$

and D-ethyl-n-amylphenylbenzylarsonium bromide was separated $[\alpha]_D = +16.5°$; $[M]_D = +70.0°$.

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ON THE SEPARATION OF THE COMPONENTS OF ALLOYS IN THE PRESENCE OF A TEMPERATURE DIFFERENCE

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(Presented by Academician G. V. Kudryumov, December 12, 1960)
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Original article submitted December 12, 1960

A number of methods are currently known for the separation of the components of a mixture; these include distillation, recrystallization, zone melting, zone purification in the solid state, and thermal diffusion. With the exception of diffusion, all of these methods are based on the different solubilities of the second component in the coexisting phases (gas–liquid, liquid–crystal, two modifications of a solid). Thermal diffusion takes place in a single phase (a mixture of gases, a solution).

In general, the thermal diffusion method is considered to be the result of a difference in the rates of movement of the components. In the present paper, we shall approach the question from the point of view of the extent to which thermal diffusion is favored. Such an approach can, without taking into account the rates of movement of the component atoms, provide an answer to the question of to what limits and in what direction can the process proceed?

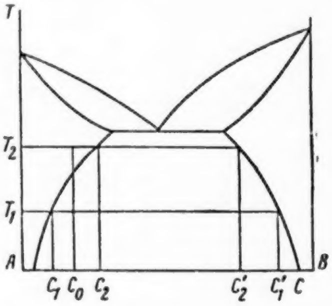

Fig. 1. Eutectic type equilibrium diagram.

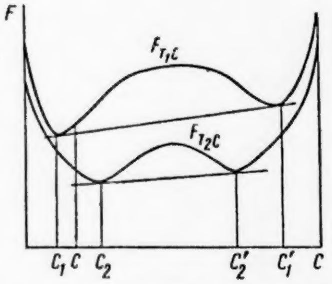

Fig. 2. Variation in free energy with concentration at two temperatures T_1 and T_2 (see Fig. 1).

First, we shall investigate whether the process of redistribution of impurities in an initially homogeneous solid body is energetically favored when a heated zone is present. We shall assume that one part of the body (a rod) is at a low temperature (T_1), and the second part is at a higher temperature (T_2). For concreteness, we shall consider the case of limited solubility of the components in the solid state. We shall denote the initial concentration of impurity in the rod by C_0; the concentration of the impurity in the solid body being purified will be denoted by C_1 at a temperature T_1 and by C_2 at a temperature T_2 (Fig. 1). We shall require that the condition $C_1 < C_0 < C_2$ (an increase in solubility with an increase in temperature) be satisfied. One could also consider the other case: $C_1 < C_0 < C_2'$. Let us consider the change in free energy when heating a part of the body to the temperature T_2 causes redistribution of the impurity in a manner such that the impurity concentration in the cold part of the rod decreases and approaches as a limit the solubility (C_1) at the temperature T_1, and the impurity content in the hot part of the rod increases and approaches as a limit the solubility (C_2) at the temperature T_2.

In the case of limited solubility, the dependence of the free energy of the mixture on concentration has the form shown in Fig. 2. At the temperature T_1, the equilibrium solubilities are C_1 and C_1', while at the temperature

T_2 they are T_2-C_2 and C_2'. The change in free energy upon redistribution of the impurity is:

$$\Delta F = \frac{1}{2}\left(F_{T_1,C_1} + F_{T_2,C_2} - F_{T_1,C_0} - F_{T_2,C_0}\right). \tag{1}$$

(The subscripts denote the free energies at the indicated temperatures and concentrations).

In accordance with the lever rule, we find:

$$F_{T_1,C_0} = \frac{C_1' - C_0}{C_1' - C_1} F_{T_1,C_1} + \frac{C_0 - C_1}{C_1' - C_1} F_{T_1,C_1'}. \tag{2}$$

Substituting this expression (1) and simplifying, we obtain:

$$2\Delta F = -\frac{C_0 - C_1}{C_1' - C_1}\left(F_{T_1,C_1'} - F_{T_1,C_1}\right) - \left(F_{T_2,C_0} - F_{T_2,C_2}\right). \tag{3}$$

It is apparent from Eq. (3) that under given conditions the free energy can decrease ($\Delta F < 0$) for certain ratios of the values in Eq. (3), and the process of redistribution of the impurity will be energetically favored. In particular, this will occur for $F_{T_1,C_1'} > F_{T_1,C_1}$ and $F_{T_2,C_0} > F_{T_2,C_2}$ (these conditions are sufficient but not necessary).

Effective purification of the cold end of the rod will take place up to the limiting value of the solubility of the impurity at the temperature of that part of the rod. Further redistribution is possible up to those values of C_1 and C_2 at which ΔF becomes zero.

It follows from the above considerations that in calculating a zone melting process it is necessary to take into account possible redistribution associated with the temperature difference along the sample being purified as well as the process usually considered – redistribution associated with the difference in the solubilities of the impurities in the liquid and solid phases.

The above consideration is also applicable to liquid mixtures.

Equation (3) may be applied to specific problems by replacing the free energy $F_{T,C}$ with a function expressing its dependence on concentration and temperature.

THE PROTONIC LABILITY OF THE HYDROGEN ATOMS IN ACETYL CHLORIDE

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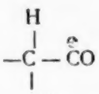
Experimental data are now available to confirm that the hydrogen atoms at α-carbons in aliphatic carbonium ions exhibit protonic lability [1]. It appeared of interest to determine whether the hydrogen atoms of acyl carbonium ions of the type



(I)

also exhibit protonic lability. Acyl carbonium ions are relatively stable particles. As early as 1922, Meerwein and Maier-Hüser established that acyl halides form solid compounds with salts of coordinationally unsaturated metals (Lewis acids) [2]. In 1947, Seel and Bauer [3] investigated these reactions by conductometric titration in liquid sulfur dioxide. They found that the addition of antimony pentachloride to acetyl chloride down to an equimolar ratio of the two substances caused a rapid increase in the electrical conductivity. The increase in electrical conductivity practically ceased as soon as an equimolar ratio was reached. These data led the authors to the conclusion that the interaction of acetyl chloride with antimony pentachloride yields an ionized substance in accordance with the following equation:

$$CH_3-COCl + SbCl_5 = [CH_3-\overset{\oplus}{C}O] + [SbCl_6]^{\ominus}.$$

In 1959, the structure of this and other similar addition products received persuasive confirmation in the work of Sandhu and co-workers [4].

Thus, salts containing an acyl carbonium ion can be easily prepared. The solution to our problem was sought in a study of isotopic hydrogen exchange between acetyl chloride and deuterium chloride in the presence of Lewis acids.

On the basis of the work discussed above, it would be expected that if the hydrogen atoms of the acyl carbonium ion (I) are actually capable of entering into an isotope exchange reaction, then the addition of a Lewis acid to the acyl chloride should promote this reaction.

Table 1 presents the results of our investigation of the kinetics of isotope exchange of hydrogen between acetyl chloride and deuterium chloride in the presence and in the absence of Lewis acids. The reaction was carried out at 25°. The acetyl chloride was dissolved in nitrobenzene, in which the DCl and the Lewis acid had previously been dissolved. The molar ratios of these components were 1 : 5 : 0.2 : 0.05, respectively. The rate constants were calculated for first order kinetics.

The data of Table 1 show that the expected effect does indeed occur. This confirms that the hydrogen atoms in acyl carbonium ions do exhibit protonic lability.

It is interesting that the rate of hydrogen–deuterium exchange between acetyl chloride and DCl in nitrobenzene solution in the presence of Lewis acids is significantly lower than the rate of hydrogen exchange by alkyl chlorides under the same conditions [5]. Thus, for example, the rate of hydrogen–deuterium exchange between isopropyl

chloride and DCl in nitrobenzene solution in the presence of 5 mole % $FeCl_3$ at 25° was so high that it was practically impossible to measure it, while the rate constant for hydrogen exchange by acetyl chloride under the same conditions was only $28 \cdot 10^{-1}$ sec^{-1}. This fact is probably explained by the structural peculiarities of acyl carbonium ions; the positive charge is distributed between the carbonyl carbon and its attached oxygen in these ions.

TABLE 1.

Lewis acid	$K \cdot 10^6$, sec^{-1}
None	1
$HgCl_2$	5
BF_3	9
$AlCl_3$	12
$FeCl_3$	28

TABLE 2.

Time, min	E.d.c.w.* of acetyl chloride, γ/ml		$K_{h.e.} \cdot 10^6$, sec^{-1}**
	calcd.	found	
1040	5010	595	0,92
1330	5010	738	1,13
4070	5010	1418	1,08
5590	5010	2204	1,56

*E.d.c.w. – excess density of combustion water.

**h.e. – hydrogen exchange. Publisher's note.

TABLE 3.

Time, min	E.d.c.w. of acetyl chloride, γ/ml		$K_{h.e.} \cdot 10^6$, sec^{-1}
	calcd.	found	
125	4900	948	29
185	4900	1250	27
240	4900	1600	27
1385	4900	4960	—

TABLE 4

$MeHal_x$	$K_{h.e.} \cdot 10^6$, sec^{-1}
None	1
$SnCl_4$	17
BF_3	25
$AlCl_3$	25
$SbCl_5$	26
$FeCl_3$	44

The data of Table 1 show that Lewis acids of different strengths accelerate isotopic hydrogen exchange by acetyl chloride to different extents. A similar phenomenon was observed during out study of hydrogen–deuterium exchange by alkyl halides [6]. Lewis acids may be arranged in series with respect to their effect on hydrogen–deuterium exchange by acetyl chloride and by alkyl halides, and the series is the same in the two cases.

It is also interesting to note that acetyl chloride is capable of hydrogen exchange in the absence of Lewis acids, although the exchange is very slow. It is probable that in this case hydrogen exchange is associated with ionization of the acetyl chloride molecule.

EXPERIMENTAL*

The acetyl chloride (b. p. 50-51°) was purified by distillation in a column with an efficiency of 30 theoretical plates. Traces of hydrogen chloride were removed by the addition of dimethylaniline to the distillation kettle.

The nitrobenzene and the Lewis acids (ferric chloride, antimony pentachloride, aluminum chloride, stannic chloride, boron trifluoride, and mercuric chloride) were purified by the same methods used in the experiments with alkyl chlorides [5].

Hydrogen–deuterium exchange experiments with acetyl chloride. Weighed amounts of the Lewis acids were dissolved in nitrobenzene (saturated with deuterium chloride) in an atmosphere of dry nitrogen; the addition was carried out in a special chamber [5]. The solution was placed in a thermostatted bath, the acetyl chloride was added, and at specific time intervals a part of the solution was transferred (under an atmosphere of dry nitrogen) to a distillation flask. The acetyl chloride was vacuum distilled from the samples at the same temperature at which the experiment was carried out. Traces of hydrogen (deuterium) chloride were removed from the acetyl chloride by treatment with dimethylaniline. The acetyl chloride was then distilled under vacuum and purified by repeated "freezing out," under vacuum, in cells cooled by solid carbon dioxide. In order to avoid contact of the acetyl chloride with atmospheric moisture, a quartz ampoule having a volume of 0.1-0.2 ml was placed in the last cell and filled with acetyl chloride. The contents of the ampoule were burned in a stream of dry oxygen, and the deuterium content of the combustion water was determined.**

We present a detailed description of the kinetic experiments for two examples.

a. Hydrogen–deuterium exchange between acetyl chloride and DCl in nitrobenzene. A solution of 8.27 g (105.3 mM) of acetyl chloride in 60.97 g of nitrobenzene containing 1.4% deuterium chloride (495.7 mM of nitrobenzene and 22 mM of DCl with an excess density of 80,000 γ/ml) was prepared. The solution was placed in a thermostatted bath at 25°, and samples of 15-20 ml were taken at specific intervals of time. The acetyl chloride was separated from these samples by the method indicated above. The results are presented in Table 2.

*L. E. Andreeva participated in the experimental work.

**The isotope analyses were carried out by N. V. Kislyakov and N. F. Mironov.

b) Hydrogen–deuterium exchange between acetyl chloride and DCl in nitrobenzene in the presence of $FeCl_3$. A solution of 1.07 g (6.6 mM) of anhydrous ferric chloride in 80.17 g of nitrobenzene containing 1.12 g of DCl (642.7 mM of nitrobenzene and 30 mM of DCl, e.d.c.w. 80,000 γ/ml) was prepared. To this solution was added 10.93 g (139.2 mM) of acetyl chloride. The mixture was placed in a thermostatted bath at 25°, and samples were collected as in the preceding experiment (see Table 3).

c) Hydrogen–deuterium exchange between acetyl chloride and DCl in nitrobenzene in the presence of $MeHal_x$. The results of the experiments on hydrogen–deuterium exchange between acetyl chloride and DCl in nitrobenzene solution in the presence of various Lewis acids are presented in Table 4. The mole ratios of the components were 1 : 5 : 0.3 : 0.1, respectively.

d) Hydrogen–deuterium exchange between acetyl chloride and DCl. Deuterium chloride was passed into freshly distilled acetyl chloride at room temperature. After 3 days, the solution was treated with dimethylaniline, and the acetyl chloride was purified in the usual manner. The e.d.c.w. was 1720 γ/ml.

These isotope exchange experiments have shown that the hydrogen atoms in acetyl chloride exhibit protonic lability and enter into hydrogen–deuterium exchange with deuterium chloride. It was established that the rate of hydrogen–deuterium exchange is significantly increased in the presence of Lewis acids; $FeCl_3$ has the greatest accelerating effect, and $HgCl_2$ has the least.

Our experimental data are in agreement with the concept that hydrogen–deuterium exchange by acetyl chloride is due to the formation of acetyl carbonium ions.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

THE RELATIVE DEHYDROGENATING ABILITIES OF SOME DIARYLPICRYLHYDRAZYL RADICALS

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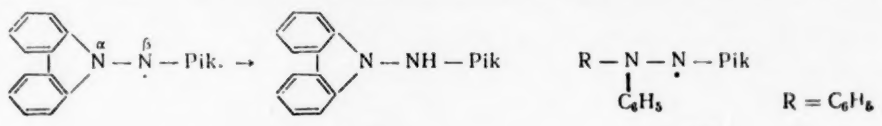
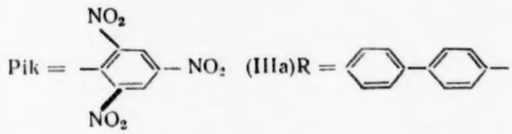
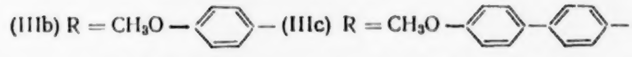
In some earlier work with picrylhydrazyl radicals, we noted that N-carbazylpicrylnitrogen [N-picryl-9-aminocarbazyl] (I) dehydrogenates hydroquinone and aromatic amines much more rapidly than does α,α-diphenyl-β-picrylhydrazyl (III); during the reaction the dehydrogenation resulting in the formation of N-carbazylpicrylamine (II) [1].



(I) (II) (III)





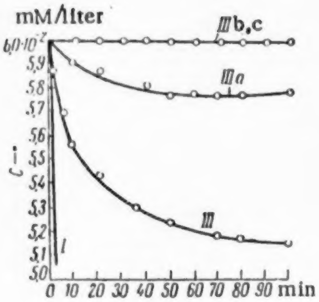
In a more detailed study of the properties of N-picryl-9-aminocarbazyl (I), it was found that this radical not only dehydrogenates the compounds indicated above, but also dehydrogenates benzene, a reaction which cannot be accomplished with radical (III). The dark violet benzene solution of radical (I) became orange [the color of amine (II)] after several minutes. When a freshly prepared solution of the radical in benzene was chromatographed on Al_2O_3 an orange colored substance was formed upon contact of the solution with the adsorbent. Elution of this material with excess benzene and evaporation of the benzene yielded a substance with an m. p. of 239-241°, which was identified as N-carbazylpicrylamine (II) by mixed melting point.

The highly effective dehydrogenating properties of radical (I) indicates a greater localization of its unpaired electron at the β-nitrogen atom than is the case in radical (III). Evidently, this is connected with the coplanarity of the α-nitrogen atom and the carbazyl system, so that there is a greater tendency for the nitrogen electrons to enter into conjugation with the π-electrons of the benzene rings than is the case with (III). In connection with this, there is less interaction of the electrons of the α-nitrogen atom with the unpaired electron of the β-nitrogen. This is in agreement with data obtained by analysis of the hyperfine structure of the electron paramagnetic resonance spectra of radicals (I) and (III), according to which the unpaired electron in radical (III) is equally distributed between the α- and β-nitrogen atoms, while it is shifted away from one of them in the case of radical (I) [2]. Therefore, it seemed of possible interest to characterize the dehydrogenating abilities of hydrazyl radicals containing residues of different structures (III, IIIa, IIIb, and IIIc).

Radicals (IIIb and IIIc) were prepared for the first time, while radical (IIIa) has been previously described. The radicals were synthesized by a method which has been described in detail in preceding communications [1, 3, 4] according to:

$$R-NH_2 \xrightarrow{o\text{-}Cl-C_6H_4COOH} \underset{\displaystyle C_6H_4-COOH}{R-NH} \rightarrow \underset{\displaystyle C_6H_5}{R-NH} \rightarrow \underset{\displaystyle C_6H_5}{R-N}-N=O$$

$$\rightarrow \underset{\displaystyle C_6H_5}{R-N}-NH_2 \xrightarrow{\text{picryl chloride}} \underset{\displaystyle C_6H_5}{R-N}-NH-Pik \xrightarrow{PbO_2} \underset{\displaystyle C_6H_5}{P-N}-N-Pik$$



Reaction rate curves for the dehydrogenation of diphenylamine by the radicals: N-picryl-9-aminocarbazyl (I); diphenylpicrylhydrazyl (III); biphenylphenylpicrylhydrazyl (IIIa); p-monomethoxydiphenylpicrylhydrazyl (IIIb); p-methoxybiphenylphenylpicrylhydrazyl (IIIc).

Analyses and constants of the previously undescribed intermediates and final products are presented in Table 1.

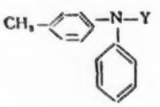
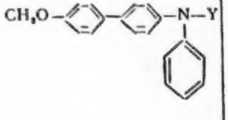
All of the radicals were deeply colored substances. Chloroform solutions of the radicals did not change color on standing in air for a period of several hours; this was confirmed by photocolorimetric measurements on the solutions.

When diphenylamine was added to solutions of the hydrazyls, dehydrogenation of the amine took place at rates depending on the structure of the radical, and the radical was converted to an orange-colored hydrazine. This permitted us to trace the course of the dehydrogenation by means of photocolorimetric measurements on the solutions. (FÉK-M photocolorimeter, concentration of radical in the solution, $6\cdot10^{-2}$ mM/liter; concentration of diphenylamine, $6\cdot10^{-1}$ mM/liter; experiment temperature, 40.0°; Wobser thermostat).

The results of the photocolorimetric measurements, which indicate the relative rates of dehydrogenation of the diphenylamine by the different radicals, are shown in Fig. 1.

It is apparent from the curves of Fig. 1 that, under the conditions of the experiments, diphenylamine is more actively dehydrogenated by carbazyl radical (II), and is not dehydrogenated by radicals (IIIb and IIIc), which contain methoxy groups. The electron-donor effect of the methoxy group evidently increases the electron density at the α-nitrogen atom, which causes greater interaction of the unpaired electron of the β-nitrogen atom with the electrons of the α-nitrogen; i.e., there is greater delocalization of the unpaired electron, and, therefore, the reactivity of these radicals is lower and their stability is higher. Naturally, in addition to the electronic effect of the groups, there is also a steric effect of the groups. These complex interactions between electronic and steric effects, on the one hand, and the stabilities of picrylhydrazyl radicals, on the other, will presumably develop as new experimental data are obtained.

TABLE 1

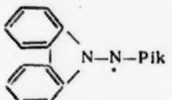
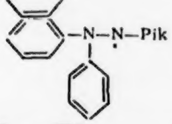
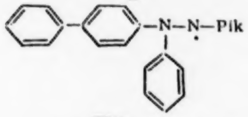
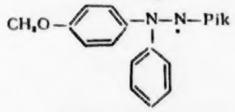
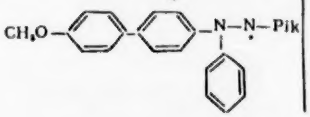
Compound	Y	M.p., °C	Yield, %	Form of crystals under the microscope	Empirical formula	N, % found	N, % calc.
	—NO	81—82	80	Ash colored prisms	$C_{13}H_{12}O_2N_2$	12.55	12.27
	—NH₂ → $-NH_2$	43—46	30	Colorless plates	$C_{13}H_{14}ON_2$	13.19	13.08
	—NH—Pik	132—133	70	Red prisms	$C_{19}H_{15}O_6N_5$ *	16.27	16.47
	—N—Pik	96—97	75	Almost black plates	$C_{19}H_{14}O_6N_5$	16.38	16.50
	$-COCH_3$	128—130	45	Colorless needles	$C_{21}H_{19}O_2N$	4.53	4.41
	—NH	140—141	80	Lustrous mother-of-pearl plates	$C_{19}H_{17}ON$	5.17	5.09
	—NO	139—140	60	Long lettuce-colored needles	$C_{19}H_{16}O_2N_2$	9.48	9.21
	$-NH_2$	148—150	25	Coarse colorless needles (clusters)	$C_{19}H_{18}ON_2$	9.89	9.65
	—NH—Pik	110—112	55	Brick-colored plates	$C_{25}H_{19}O_7N_5$ **	13.81	13.97
	—N—Pik	105—107	40	Almost black fine prisms	$C_{25}H_{18}O_7N_5$	14.16	14.00

* Found %: C 53.47; H 3.61. Calculated %: C 53.65; H 3.55.

** Found %: C 59.78; H 3.98. Calculated %: C 59.88; H 3.82.

Table 2 presents the results of measurements of line widths of e.p.r. spectra of the radicals between points of maximum slope, $\Delta H_{m.s.}$. The measurements were carried out in weak fields, H_0 = 20 oe, on crystalline samples of the radicals; the apparatus has been described previously [5]. It is apparent from the data of the table that the absorption line widths, which characterize the magnitude of the exchange interactions of the unpaired electrons in the crystalline material, may be arranged in the same order as the results of the photocolorimetric evaluation of the dehydrogenation of diphenylamine by these same radicals.

TABLE 2

Radical	$\Delta H_{m.s.}$
	0,52±0,01
	1,0±0,01
	1,11±0,01
	2,6±0,01
	7,3±0,01

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REACTIONS OF HALOGEN DERIVATIVES OF ETHYL- AND ACETYLFERROCENE

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The present work was devoted to a study of the substitution of nucleophilic groups for bromine in 1'-bromo-1-acetylferrocene and 1'-bromo-1-ethylferrocene in the presence of copper salts. The 1'-bromo-1-acetylferrocene was prepared by acetylation of bromoferrocene with acetic anhydride in the presence of phosphoric acid; the method was similar to that used for the preparation of acetylferrocene [1]. The yield was 54%.

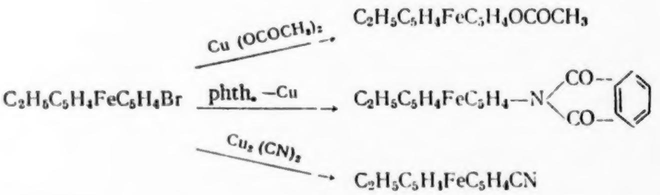
$$C_5H_5FeC_5H_4Br \xrightarrow[H_3PO_4]{(CH_3CO_2)O} CH_3COC_5H_4FeC_5H_4Br.$$

The acetyl group and the bromine were in different rings, as confirmed by the absence from the i.r. spectrum of frequencies at 1000 and 1100 cm^{-1} which are characteristic of ferrocene compounds with an unsubstituted cyclopentadienyl ring.

It was found that the bromine in this compound is replaced by an acetoxy group with much more difficulty than is the bromine in bromoferrocene [2]; even a five-hour refluxing of the reactants in aqueous alcohol does not cause complete disappearance of the halogen. In order to separate the reaction product from unreacted 1'-bromo-1-acetylferrocene, the reaction mixture was hydrolyzed, and the resulting 1'-hydroxy-1-acetylferrocene was separated; the latter was easily benzoylated by means of the Schotten-Baumann reaction.

$$CH_3COC_5H_4FeC_5H_4Br \xrightarrow[2.\ KOH]{1.\ Cu\ (OCOCH_3)_2} CH_3COC_5H_4FeC_5H_4OH \xrightarrow{KOH,\ C_6H_5COCl} CH_3COC_5H_4FeC_5H_4OCOC_6H_5$$

If the 1'-bromo-1-acetylferrocene is first reduced, which may be very easily (within 5 min) accomplished by Clemmensen reduction, the halogen in the resulting 1'-bromo-1-ethylferrocene has approximately the same lability as the bromine in bromoferrocene; it is easily replaced by acetoxy, phthalimido, and cyano groups by heating with the corresponding copper salts:



1'-Acetoxy-1-ethylferrocene, like ferrocenyl acetate [3], is hydrolyzed by alkali with the formation of 1'-hydroxy-1-ethylferrocene, which undergoes Schotten-Baumann benzoylation to 1'-benzoyl-oxy-1-ethylferrocene. 1-Cyano-1'-ethylferrocene was hydrolyzed to 1'-ethylferrocene-1-carboxylic acid, which was identical to the acid prepared by N. A. Nesmeyanov and O. A. Reutov [4] by reduction of 1'-acetyl-1-carboxylic acid.

1'-Phthalimido-1-ethylferrocene was converted to 1'-amino-1-ethylferrocene by heating with hydrazine hydrate; this liquid was acetylated to 1'-acetamido-1-ethylferrocene.

EXPERIMENTAL

1'-Bromo-1-acetylferrocene. A mixture of 10 g of bromoferrocene, 40 ml of acetic anhydride, and 10 ml of phosphoric acid (from 2 parts of 85% H_3PO_4 and 1 part of P_2O_5) was heated, with stirring, on a boiling water bath for 5 min, cooled with ice, and poured into a solution of sodium carbonate. After neutralization, the mixture was extracted with ether, and the ether extract was filtered, washed with water, and dried over $MgSO_4$. The ether was distilled. The residue was dissolved in a small amount of benzene, and the solution was diluted with petroleum ether and chromatographed on Al_2O_3. The unreacted bromoferrocene was eluted with petroleum ether, and the 1'-bromo-1-acetylferrocene was eluted with benzene or ether. There was obtained 6.2 g of 1'-bromo-1-acetylferrocene (54% of theoretical) with an m. p. of 61.5-63° (from hexane). The ketone was readily soluble in benzene, ether, and alcohol; it was difficultly soluble in petroleum ether.

Found %: C 47.21, 47.22; H 3.82, 3.70; Br 25.46, 25.76; Fe 18.26, 18.15. $C_{12}H_{11}FeOBr$. Calculated %: C 46.95; H 3.61; Br 26.03; Fe 18.20.

The oxime melted at 109.5-111.5° (from aqueous alcohol).

Found %: C 44.68, 44.79; H 3.78, 3.76; Br 25.02, 25.20; Fe 17.80, 17.81; N 4.07, 4.12. $C_{12}H_{12}FeOBrN$. Calculated %: C 44.76; H 3.76; Br 24.82; Fe 17.34; N 4.35.

1'-Hydroxy-1-acetylferrocene. To a boiling solution of 1.0 g of 1'-bromo-1-acetylferrocene in 20 ml of alcohol was added a hot solution of 3 g of copper acetate in 20 ml of water, and the mixture was refluxed under nitrogen on a water bath for 40 min. The mixture was then diluted with water and extracted with ether, and the ether extract was washed with a small amount of water and dried over $MgSO_4$. The ether was distilled, and the remaining oil gave a positive test for halogen. It was hydrolyzed by boiling (10 min) under nitrogen in a solution of 5 ml of alcohol and 10 ml of 10% KOH. The alcohol was distilled. The unreacted ketone was extracted with ether, and 0.23 g of ketone was obtained. CO_2 was passed through the alkaline solution; the 1'-hydroxy-1-acetylferrocene was extracted with ether, and the ether extracted was washed with a small amount of water and distilled under nitrogen. The residue was crystallized from water under N_2. There was obtained 0.21 g of 1'-hydroxy-1-acetylferrocene (26% of theoretical) with an m. p. of 115.5-118.5° (under nitrogen).

Found %: C 58.65, 58.51; H 5.02, 5.08; Fe 23.09, 23.09. $C_{12}H_{12}FeO_2$. Calculated %: C 59.05; H 4.96; Fe 22.88.

This compound was somewhat more stable in air than hydroxyferrocene; it oxidized readily in solution.

1'-Benzoyloxy-1-acetylferrocene. 1'-Hydroxy-1-acetylferrocene (0.21 g) was dissolved in 10 ml of 10% KOH and subjected to Schotten-Baumann benzoylation with 0.5 ml of benzoyl chloride. There was obtained 0.23 g of 1'-benzoyloxy-1-acetylferrocene (77% of theoretical); m. p. 84-85° (from a 2:1 mixture of cyclohexane and hexane).

Found %: C 65.50, 65.74; H 4.66, 4.67; Fe 16.07, 15.83. $C_{19}H_{16}O_3Fe$. Calculated %: C 65.54; H 4.63; Fe 16.04.

1'-Bromo-1-ethylferrocene. Eight grams of zinc dust was amalgamated with 0.8 g of mercuric chloride in 32 ml of dilute HCl (1:20). After 10 min the liquid was decanted, and a solution of 2.0 g of 1'-bromo-1-acetylferrocene in 20 ml of acetic acid and 20 ml of concentrated HCl was added. The mixture was refluxed for about 5 min, until the dark cherry color of the ketone disappeared. The mixture was then cooled and filtered from the zinc, and the zinc was washed with ether. The filtrate was diluted with water and extracted with ether. The combined ether extracts were washed with water, 10% KOH, and again with water, and the ether was distilled. The residue was dissolved in n-hexane and chromatographed on Al_2O_3; the hexane was distilled, and the substance was distilled under vacuum. There was obtained 1.46 g (77% of theoretical) of 1'-bromo-1-ethylferrocene. B. p. 110-112° (1.2 mm); $n^{20}D$ 1.6238, d^{20}_4 1.5584.

Found %: C 49.42, 49.35; H 4.55, 4.54; Br 27.34, 27.23; Fe 19.28, 19.58. $C_{12}H_{13}FeBr$. Calculated %: C 49.18; H 4.47; Br 27.28; Fe 19.06.

Exchange of the halogen in 1'-bromo-1-ethylferrocene for a hydroxy group. 1'-Benzoyloxy-1-ethylferrocene. To a boiling solution of 1.3 g of 1'-bromo-1-ethylferrocene in 35 ml of alcohol was added a hot solution of 3.5 g of copper acetate in 35 ml of water, and the mixture was refluxed on a water bath for 15 min. The reaction mixture was diluted with water and extracted with ether, and the ether extract was washed with water, 5% KOH, and again with water and dried over $MgSO_4$. The ether was distilled. The residual oil did not contain halogen. Since

1'-acetoxy-1-ethylferrocene undergoes change when distilled under a vacuum of 1.2 mm, it was not distilled for use in subsequent work.

A solution of 0.3 g of 1'-acetoxy-1-ethylferrocene in 4 ml of alcohol and 4 ml of 10% KOH was refluxed for 15 min; the alcohol was distilled, and the solution was cooled and filtered. When CO_2 was passed into the solution, 1'-hydroxy-1-ethylferrocene separated as a liquid. It was again dissolved in alkali and subjected to Schotten-Baumann benzoylation. There was obtained 0.26 g (71% of theoretical) of 1'-benzoyloxy-1-ethylferrocene; m. p. 42.5-44.5° (from methanol, with dry ice cooling).

Found %: C 68.33, 68.27; H 5.43, 5.44; Fe 16.75, 16.54. $C_{19}H_{18}FeO_2$. Calculated %: C 68.28; H 5.43; Fe 16.71.

1'-Phthalimido-1-ethylferrocene. A mixture of 0.5 g of 1'-bromo-1-ethylferrocene and 1.5 g of copper phthalimide was heated under nitrogen at 135-140° for 1.5 hr. The mixture was then repeatedly washed with ether. The ether extract was carefully washed with 10% KOH and with water and dried over $MgSO_4$. The ether was distilled. The remaining dark red oil did not contain halogen; it crystallized when dried under vacuum over P_2O_5. There was obtained 0.44 g (72% of theoretical) of 1'-phthalimido-1-ethylferrocene with an m. p. of 81.5-82.5° (from methanol).

Found %: C 66.90, 66.72; H 4.75, 4.75; Fe 15.78, 15.67; N 4.06, 3.90. $C_{20}H_{17}FeO_2N$. Calculated %: C 66.87; H 4.77; Fe 15.55; N 3.90.

1'-Acetamido-1-ethylferrocene. A solution of 0.4 g of 1'-phthalimido-1-ethylferrocene in 6 ml of alcohol was refluxed under nitrogen with 0.6 ml of hydrazine hydrate for 30 min. The mixture was diluted with water and extracted with ether, and the ether extract was washed with 10% KOH and with water. The amine was extracted with 10% HCl, and, upon the addition of alkali to the extract, 1'-amino-1-ethylferrocene separated as an oil; the amine was extracted with ether. Distillation of the ether yielded 0.19 g (77% of theoretical) of the amine, and this was acetylated with 0.7 ml of acetic anhydride in 1.5 ml of absolute pyridine. There was obtained 0.19 g (85% of theoretical) of 1'-acetamido-1-ethylferrocene; m. p. 69.5-70.5° (from a 2:1 mixture of benzene and hexane).

Found %: C 62.15, 62.05; H 6.37, 6.52; Fe 19.90, 19.90; N 5.48, 5.32. $C_{14}H_{17}FeNO$. Calculated %: C 62.01; H 6.32; Fe 20.60; N 5.17.

1-Cyano-1'-ethylferrocene. A mixture of 0.4 g of 1'-bromo-1-ethylferrocene and 1.5 g of copper cyanide was heated under nitrogen at 135-140° for 50 min. The reaction mixture was washed with ether, the ether was evaporated, and the residue was chromatographed on Al_2O_3. The 1'-cyano-1-ethylferrocene was eluted with benzene. There was obtained 0.26 g (80% of theoretical) of 1-cyano-1'-ethylferrocene with an m. p. of 28-29° (from hexane, with dry ice cooling).

Found %: C 65.25, 65.25; H 5.45, 5.76; N 5.72; Fe 23.72, 23.57. $C_{13}H_{13}FeN$. Calculated %: C 65.30; H 5.48; N 5.86; Fe 23.36.

The cyano derivative was hydrolyzed by refluxing for a number of hours in aqueous alcoholic KOH. The resulting 1'-ethylferrocene-1-carboxylic acid melted at 74.5-76.5°, and a mixture with a known sample melted without depression of the melting point. The literature reports an m. p. of 75.5-77.5° [4].

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SULFONATION OF ACYL AND CARBOMETHOXY DERIVATIVES OF FERROCENE

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(Presented by Academician A. N. Nesmeyanov, October 15, 1960)
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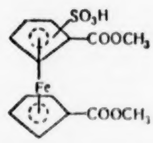
Original article submitted December 26, 1960

We recently reported the preparation of 1-carbomethoxyferrocene-1'-sulfonic acid and described a number of its derivatives [1]. In the present work, the sulfonation reaction was extended for the first time to other ferrocene compounds.

1,1'-Dicarbomethoxyferrocene was successfully sulfonated with a solution of sulfur trixoide in dichloroethane. To a solution of 0.025 mole of the ester in 50 ml of dichloroethane was added, over a period of an hour, a solution of 0.037 mole of sulfur trixoide in the same solvent at 0°. The mixture was stirred for an hour and a half at 20°, and the reaction products were extracted with water. The excess sulfuric acid was precipitated as barium sulfate by the addition of barium chloride, and the transparent solution was evaporated almost to dryness in a stream of warm air. The residual yellow crystals were separated by filtration and washed on the filter with acetone and ether. The yield was 60%, calculated on the pure sulfonic acid I. However, the sulfonic acid contained a significant amount of its iron salt, which was formed during partial decomposition of the ferrocene. Sulfonic acid I was identified in the form of the acid chloride. Acid chlorides of ferrocenesulfonic acids are readily prepared by the following method.



I

To a suspension of 0.01 g of the sulfonic acid (or its lead salt) in 15 ml of dichloroethane was added 0.05 mole of PCl_3; after 30 min, 0.015 mole of PCl_5 was added portion-wise over a period of 1 hr. The mixture was heated for an hour at 50-60° and then filtered. The solution was cooled, treated with ice water, washed twice with water and with a 1% solution of sodium carbonate, and dried over calcium chloride. The solvent was evaporated in a stream of air. The yield of ferrocene-1,1'-disulfonyl chloride was 95% (from the lead salt). The yield of the chloride of sulfonic acid I was 50%, calculated on the pure initial acid. This acid chloride was recrystallized from ether, butyl alcohol, and a mixture of these solvents (1:1). After recrystallization, it melted at 96-97°.

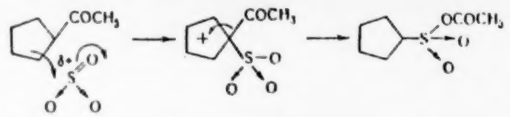
Found %: C 42.17, 42.01; H 3.38, 3.34; Fe 14.01, 13.79; Cl 8.95, 8.77. $C_{14}H_{13}O_6ClFe$. Calculated %: C 41.97; H 3.27; Fe 13.94; Cl 8.85.

The melting point had increased only insignificantly after the first recrystallization; this probably indicates that we were dealing with one of the two possible isomers which could have been formed in the sulfonation.

It seemed possible that 1,1'-diacetylferrocene would behave similarly to 1,1'-dicarbomethoxyferrocene during sulfonation. However, we were able to separate only ferrocene-1,1'-disulfonylchloride from the reaction products* after treatment with PCl_5; the yield was 25% (75% calculated on the 1,1'-diacetylferrocene reacted). Thus, both acetyl groups were replaced by sulfonic acid groups.** It is most probable that a mixed anhydride was first formed in accordance with the following scheme:

* Reaction conditions and method: to 0.06 mole of 1,1'-diacetylferrocene in 150 ml of dichloroethane was added, with stirring (0°), 0.09 mole of SO_3 in 100 ml of dichloroethane. After 2 hr at 0° and 2 hr at 20°, the reaction mixture was treated as described for the preparation of sulfonic acid I.

** Similar results were obtained by Krekeler in 1886 during sulfonation of acetophenone by pyrosulfuric acid [2, 3].



This anhydride hydrolyzes readily during subsequent treatment.

When larger radicals, such as phenyl or cyclohexyl, are present in the acyl group, replacement of the acyl group by a sulfonic acid group does not take place (probably as a consequence of steric hindrance). Upon treatment with sulfur trioxide in dichloroethane (under the same conditions), 1,1'-dibenzoylferrocene remained unchanged, and 1,1'-di(hexahydrobenzoyl)ferrocene was decomposed to the extent of 45%, while 40% of it was recovered unchanged. The latter of these two ketones was prepared by Friedel-Crafts synthesis with a yield of 30%. The m. p. was 135-135.5° (from alcohol).

Found %: C 71.42, 71.33; H 7.58, 7.60; Fe 13.61, 13.17. $C_{24}H_{30}O_2Fe$. Calculated %: C 70.94; H 7.44; Fe 13.74.

Acetylferrocene was sulfonated with sulfur trioxide–dioxane in dichloroethane. This gave a 50-60% yield of 1-acetylferrocene-1'-sulfonic acid. To a solution of 7 g of acetylferrocene in 50 ml of dichloroethane was added, at 0°, a suspension of sulfur trioxide–dioxane (from 3.1 g of dioxane and 3.0 g of SO_3) in 25 ml of dichloroethane. The reaction mixture was allowed to stand for an hour at 0° and for 5 hr at 20°, and the reaction products were extracted with the minimum amount of water. The extract was washed with chloroform, and the aqueous solution was then evaporated to dryness in a stream of air. The residue was washed several times with acetone, and 2.3 g of golden crystals was obtained. In all probability, the crystals were the iron salt of 1-acetylferrocene-1'-sulfonic acid. The crystals were recrystallized from acetic acid.

Found %: C 38.11, 37.92; H 4.04, 4.10; S 8.28, 8.36; Fe 22.93, 22.67. $C_{24}H_{22}S_2O_8Fe_3 \cdot 5H_2O$. Calculated %: C 37.92; H 4.24; S 8.24; Fe 22.04.

The acetone solution obtained during washing of the crystals contained free sulfonic acid. This solution was treated with excess diazomethane in ether. There was obtained 2.4 g of methyl-1-acetylferrocene-1'-sulfonate. After three recrystallizations from methanol, the material melted at 79.5-81°.

Found %: C 48.40, 48.47; H 4.36, 4.28; S 9.82, 9.84; Fe 17.70, 17.97. $C_{13}H_{14}SO_4Fe$. Calculated %: C 48.49; H 4.38; S 9.95; Fe 17.34.

The i.r. spectrum of this ester showed that the sulfonic acid group and the acetyl group were in different rings of the ferrocene molecule. Sulfonation of acetylferrocene under more vigorous conditions (an excess of sulfur trioxide, a dioxane medium, heating at 60-80°) gave ferrocene-1,1'-disulfonic acid, which was identified in the form of the methyl ester, and, in addition, 1-acetylferrocene-1'-sulfonic acid.

Thus, ferrocene derivatives containing one electrophilic substituent (–COOH or –$COOCH_3$ [1], –SO_3H [4] or –$COCH_3$) are smoothly sulfonated in the cold by sulfur trioxide–dioxane; in this case substitution takes place in the unsubstituted ring. If both rings of the ferrocene molecule contain electrophilic substituents, the reaction is hampered. Thus, an ester of ferrocene-1,1'-dicarboxylic acid is sulfonated by sulfur trioxide in dioxane but not by sulfur trioxide–dioxane. 1,1'-Diacetylferrocene is not sulfonated, but exchanges the acetyl for sulfonic acid groups. 1,1'-Dibenzoyl- and 1,1'-di(hexahydrobenzoyl)ferrocene are not sulfonated. We were unable to sulfonate ferrocene-1,1'-disulfonyl chloride, either with an excess of sulfur trioxide in dichloroethane (refluxing 3 hr) or by heating (50°) with 40% oleum.

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AN IMPROVEMENT IN THE ACCURACY OF THE CONSTANTS IN THE TATEVSKII METHOD OF CALCULATION OF HEATS OF COMBUSTION OF ALKANES

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A number of methods based on additivity have been proposed for the calculation of various physicochemical properties of the alkanes, particularly heats of combustion [1-11]. One of the most systematic of these methods and one which gives calculated values in good agreement with experimentally determined values is the method proposed by V. M. Tatevskii [6].

In this method, all C−C and C−H bonds in the alkane molecule are typed on the basis of the nature of the component carbon atoms – primary (C_1), secondary (C_2), tertiary (C_3), or quaternary (C_4). Thus, ten subtypes of carbon–carbon bonds are possible: C_1-C_1 (only in ethane), C_1-C_2, C_1-C_3, C_1-C_4, C_2-C_2, C_2-C_3, C_2-C_4, C_3-C_3, C_3-C_4, and C_4-C_4. There are three subtypes of C−H bonds: C_0-H (only in methane) C_1-H, C_2-H, and C_3-H.

Numerical values of certain properties of alkanes (refractive index, molar volume, heats of combustion and formation, etc.) can be obtained by a summation of certain constants – "contributions" – of each of the carbon–carbon bonds in the molecule in accordance with the subtypes enumerated above (in this variant, the "contributions" of the C−H bonds are included in the "contributions" of the C−C bonds).

The numerical value of the contribution of each bond subtype can be determined by comparing the corresponding relationships with experimental data.

We present below values of the contributions of the various bond subtypes for calculating the heat of combustion (at 25°) of alkanes both in the vapor and the liquid states; these values were determined by V. M. Tatevskii.

Bond subtype	C_1-C_2	C_1-C_3	C_1-C_4	C_2-C_2	C_2-C_3	C_2-C_4	C_3-C_3	C_3-C_4	C_4-C_4
Contribution									
Liquid	263,238	226,993	208,679	156,231	120,454	102,696	85,551	68,904	—
Vapor	265,17	228,48	210,01	157,41	121,35	103,35	86,45	69,40	53,22

It will be noted that the above tabulation contains no contribution for C_4-C_4 bonds to the heat of combustion of alkanes in the liquid state. At the time the method was designed, the author did not have available experimental data for any alkane with a C_4-C_4 bond in the molecule and in particular, for which the heat of combustion in the liquid state was known.* As regards the contribution of the C_4-C_4 bond for calculation of the heat of combustion of alkanes in the vapor state, this value was calculated by the author from the only experimentally determined heat of combustion available at that time – that of 2,2,3,3-tetramethylbutane. V. M. Tatevskii has repeatedly pointed out that this value cannot be considered reliable [6, 18], since the heat of combustion of this substance was determined for the solid state [13], and the heat of combustion for the vapor state was calculated by means of the heat of sublimation [14].

We have measured the heat of combustion of 2,2,3,3-tetramethylhexane in the liquid state at 25°; the value is 1619.1 ± 0.5 kcal/mole.**

* The heat of combustion of 2,2,3,3-tetramethylpentane reported by Johnson, Prosen and Rossini [12] was used by V. M. Tatevskii only in his most recent publication [18].

** The methods used for the synthesis, purification, and determination of the heat of combustion of this material have been reported in references [15, 16].

Through the use of this value together with the previously determined value of the heat of combustion of 2,2,3,3-tetramethylpentane [12] we were able to calculate the contribution of a C_4-C_4 bond to the heat of combustion of alkanes in both the liquid and the vapor state.

The results of this calculation are presented in Table 1.

Compound used to calc. the contribution	Contribution of the C_4-C_4 bond (liquid)	Contribution of the C_4-C_4 bond (vapor)
2,2,3,3-Tetramethylhexane	53.55	54.26*
2,2,3,3-Tetramethylpentane	53.77	54.32
2,2,3,3-Tetramethylbutane	–	(53.22)**
Average	53.66	54.29

* The heat of evaporation was calculated by a semiempirical relationship.
** Taken from the paper by V. M. Tatevskii [6].

It is apparent from an inspection of Table 1 that:

1. The values of the contribution of a C_4-C_4 bond to the heat of combustion of alkanes in both the liquid and the vapor state as calculated from the data obtained in the present work (from the heat of combustion of 2,2,3,3-tetramethylhexane)are in agreement with the values calculated from the data of reference [12] (from the heat of combustion of 2,2,3,3-tetramethylpentane). The deviation of about 1 kcal of the value cited by Tatevskii is probably due to inaccuracy in the value of the heat of sublimation.

2. At the present time, the most probably value of the contribution of a C_4-C_4 bond is 53.66 kcal/mole for the heat of combustion in the liquid state and 54.29 kcal/mole for the heat of combustion in the vapor state.

The use of these values will permit calculation of the heats of combustion of all alkanes having a C_4-C_4 bond in the molecule.

Using one of these values (53.66 kcal/mole), we were able to compare our experimentally determined value of the heat of combustion of 2,2,3,3,5,5,6-heptamethylheptane (2248.4 ± 0.4 kcal mole) with the value calculated by means of the additivity method of V. M. Tatevskii (2247.7 kcal/mole).* As may be seen, the agreement of the experimental and calculated values is satisfactory.

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SYNTHESIS OF MONOHYDRIC SATURATED AND ACETYLENIC TERTIARY ALCOHOLS OF THE FERROCENE SERIES

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That it is possible to prepare dihydric tertiary alcohols of the ferrocene series from carbonyl-containing derivatives of ferrocene, diacetyl- and dibenzoylferrocene, respectively, as well as from the dimethyl ester of ferrocenedicarboxylic acid has already been demonstrated by Riemschneider and Helm [1] and by A. N. Nesmeyanov and coworkers [2]. The present work represents the first time that the synthesis of monohydric saturated and acetylenic tertiary alcohols of the ferrocene series has been carried out; the synthesis was accomplished by the condensation of monoacetyl- and monobenzoylferrocenes with organomagnesium and organosodium compounds.

The saturated tertiary alcohols were synthesized by condensation of acetylferrocene and benzoylferrocene with Grignard reagents prepared from alkyl halides. Preparation of alcohols with an acetylenic radical was carried out with ethynylmagnesium bromide, which was prepared by the method of Jones [3] (we were unable to synthesize this type of alcohol by the Favorskii reaction). Sodium acetylide was prepared by the method of Normant [4], at −15°, and this was condensed with acetyl- and benzoylferrocene. The results demonstrated that 3-methyl-3-ferrocenyl-3-hydroxy-1-propyne can be prepared by two routes (through C_2HMgBr and C_2HNa), while 3-phenyl-3-ferrocenyl-3-hydroxy-1-propyne can be synthesized only by the first method.

It is interesting that organometallic derivatives of acetylene containing two metal substituents (Iotsitch reagents) do not react either with acetylferrocene or with benzoylferrocene.

The properties of these tertiary alcohols of the ferrocene series are presented in the table.

Properties of Tertiary Alcohols of the Ferrocene Series

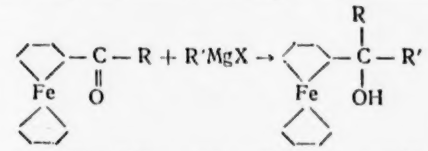
Compound	Yield, %	M.p., °C	Found, %			Empirical formula	Calculated, %		
			C	H	Fe		C	H	Fe
α-Hydroxyisopropylferrocene	58	56—58	64,01 64,10	6,39 6,40	22,20	$C_{13}H_{16}OFe$	63,97	6,56	22,90
α-Hydroxy-α-phenylethylferrocene	32	110—111	70,62 70,68	6,59 6,47	18,70	$C_{18}H_{18}OFe$	70,59	5,88	18,26
α-Hydroxy-α-phenylpropylferrocene	60	87—88	71,45 71,29	6,91 6,85	17,10	$C_{19}H_{20}OFe$	71,28	6,25	17,46
α-Hydroxy-α-phenylamylferrocene	72	65—66	72,52 72,40	6,70 6,75	16,68	$C_{21}H_{24}OFe$	72,41	6,91	16,10
3-Methyl-3-ferrocenyl-3-hydroxy-1-propyne*	5	—	66,25 66,05	6,58 6,68	—	$C_{14}H_{14}OFe$	66,14	5,51	22,04
3-Methyl-3-ferrocenyl-3-hydroxy-1-propyne**	5	112—114	65,38 65,16	5,77 5,56	22,85	$C_{14}H_{14}OFe$	66,14	5,51	22,04
3-Phenyl-3-ferrocenyl-3-hydroxy-1-propyne*	16	89—90	72,02 71,92	5,33 5,36	17,33	$C_{19}H_{16}OFe$	72,19	5,10	17,67

* Ethynylmagnesium bromide, prepared by the method of Jones [3], was used in this synthesis.

** Sodium acetylide, prepared by the method of Normant [4], was used in this synthesis.

EXPERIMENTAL

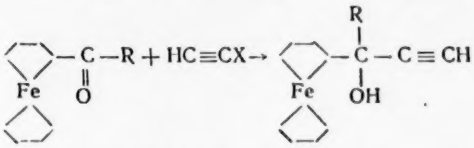
The saturated tertiary alcohols were synthesized according to the scheme:



$R = CH_3, C_6H_5 \quad R' = CH_3, C_2H_5, n\text{-}C_4H_9$

The synthesis was carried out under the conditions described in reference [1]. Acetyl- or benzoylferrocene was added to the Grignard reagent in benzene solution, and the reaction mixture was stirred for 1 hr at 60°. The mixture was then decomposed with a saturated solution of NH_4Cl. The reaction product was given a preliminary purification with activated charcoal, and was then recrystallized from dilute ethyl alcohol. The yield of reaction product was 58-72%. The following alcohols were prepared: α-hydroxyisopropylferrocene, α-hydroxy-α-phenylethylferrocene, α-hydroxy-α-phenylpropylferrocene, and α-hydroxy-α-phenylamylferrocene.

The following scheme indicates the method of synthesis of the acetylenic alcohols:



$R = CH_3, C_6H_5; \ X = MgBr, \ Na$

The ethynylmagnesium bromide was prepared by the method described in reference [3]. A solution of acetylferrocene in THF* was added to the Grignard reagent at room temperature. The reaction mixture was stirred for 12 hr, and was then decomposed with a saturated solution of NH_4Cl and extracted with ether. The ether extract was dried with Na_2SO_4. The solvent was distilled, and the residue (a dark red liquid) was dissolved in hexane and boiled with activated charcoal. The precipitated crystals were purified by recrystallization from dilute alcohol.

Condensation of ethynylmagnesium bromide with benzoylferrocene was carried out in a similar manner. Sodium acetylide was prepared by the method of Normant [4] at −15°. A solution of acetylferrocene in THF was added to this reagent at −10°. The reaction product was decomposed with a solution of NH_4Cl, and was then extracted with ether. The ether extract was dried over Na_2SO_4, and the solvent was distilled. The residue was chromatographed on Al_2O_3. A fraction with a b. p. of 112-114° was separated. This was shown to be an acetylenic alcohol.

The following alcohols were prepared: 3-methyl-3-ferrocenyl-3-hydroxy-1-propyne (by two routes – through C_2HMgBr and through C_2HNa) and 3-phenyl-3-ferrocenyl-3-hydroxy-1-propyne.

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* THF – tetrahydrofuran. Publisher's note.

CONVERSION OF AMINES OF THE FURAN SERIES TO PYRROLIDINE HOMOLOGS

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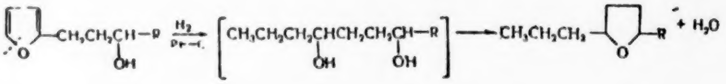
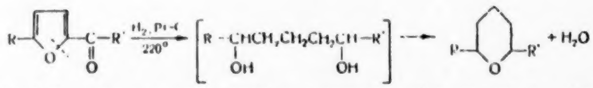
Hydrogenolysis of the furan ring generally leads to aliphatic compounds, the ether oxygen of the ring forming a carbonyl or hydroxyl group. In the case of 2-alkyl- or 2,5-dialkylfurans, the products of ring hydrogenolysis are alcohols or ketones depending on the reaction conditions. New possibilities for the course of the reaction have been discovered in the case of the hydrogenation of furan compounds containing a side chain in the α-position with a functional group capable, under certain conditions, of interacting intramolecularly with the carbonyl or hydroxyl group formed by hydrogenolysis of the furan ring. Such a functional group may be a hydroxyl group, for example, located in the 3-position with respect to the furan ring. We have previously investigated the hydrogenolysis of furan compounds having this structure, specifically, 1-furyl-3-alkanols [1]. This work showed that when the reaction is carried out under hydrogenation conditions in a flow system over a platinum catalyst, the primary products of hydrogenolysis of the furan ring are 1,4-alkanediols, which, as a result of intramolecular elimination of water, are converted to tetrahydrofurans:

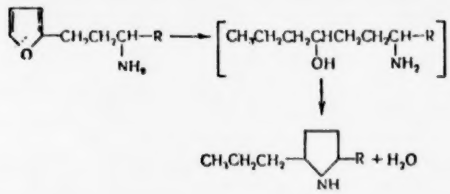


Another and similar case is that of 2-alkyl-5-acylfurans. In this case, however, it must be remembered that there are two possible courses along which this reaction can take place; these are connected with the circumstance that the primary reaction during hydrogenation can be either reduction of the carbonyl group to a CH_2 group [2] or hydrogenolysis of the furan ring. It is possible to accomplish hydrogenolysis of the furan ring before reduction of the carbonyl group by using a platinum catalyst [3]. In the latter case, the primary products of hydrogenolysis of 2-alkyl-5-acetylfurans are 1,5-diketones and 1,5-diols, which, under vapor-phase hydrogenation conditions, are cyclized with the elimination of water to six-membered carbocyclic compounds and tetrahydropyrans [4].



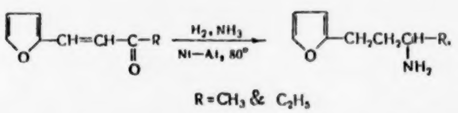
The general concept of both of the above cases may be expressed as follows: If the side chain of the furan compound contains a functional group capable of reacting with the hydroxyl or carbonyl group formed during hydrogenolysis of the furan ring, and if a γ- or δ-bifunctional aliphatic compound is formed as a result of hydrogenolysis of the furan ring, then hydrogenation of the furan compound under specific conditions leads to new five- or six-membered heterocyclic compounds.

This general concept immediately suggests the possibility of carrying out new and interesting syntheses. In actual practice, the functional group capable of interaction with the hydroxyl or carbonyl group may be an amino group, and, therefore, it would be expected that amines of the furan series having the NH_2 group in the 3-position with respect to the furan ring would be converted, under hydrogenation conditions, to five-membered nitrogen-containing heterocyclic compounds — pyrroles or pyrrolidines; i.e., the following reaction would be expected to take place:



The experiments carried out in the present work completely confirmed our assumption. We synthesized two amines of the furan series, 1-furyl-3-aminobutane and 1-furyl-3-aminopentane, and these were subjected to hydrogenation over a platinum catalyst in a flow system. The reactions yielded 2-methyl-5-n-propylpyrrolidine and 2-ethyl-5-n-propylpyrrolidine in yields of 70-80%.

Synthesis of the 1-furyl-3-aminoalkanes. The 1-furyl-3-aminobutane and 1-furyl-3-aminopentane were prepared by reductive amination of the corresponding furfurylidine ketones in the liquid phase over skeletal Ni/Al catalyst.



The method used for the reductive amination of the furfurylidene ketones was similar to that used for the amination of 2-furaldehyde [5]. The resulting 1-furyl-3-aminoalkanes, which were obtained in yields of 70-75%, were distilled under reduced pressure:

1. 1-Furyl-3-aminobutane: b. p. 94-96° (25 mm); $n^{20}D$ 1.4760, d^{20}_4 0.9664.
2. 1-Furyl-3-aminopentane: b. p. 98-99° (17 mm); $n^{20}D$ 1.4786, d^{20}_4 0.9586.

Conversion of the 1-furyl-3-aminoalkanes to 2-n-propyl-5-alkylpyrrolidines. The 1-furyl-3-aminoalkanes were hydrogenated in a flow system at a space rate of 0.1 hr^{-1}; the catalyst was platinum deposited on carbon. The temperature inside the catalyst bed was maintained within the interval of 200-210°. The catalyst was prepared as follows: Activated carbon was impregnated with chloroplatinic acid, placed in the reaction tube, and the chloroplatinic acid was reduced with hydrogen for 13 hr as the temperature was gradually increased from 250 to 320°. The catalyzates were saturated with KOH, separated from the water layer, dried with calcined KOH, and distilled in an efficient column. The pyrrolidines obtained by this distillation were again distilled over sodium from a flask fitted with a dephlegmator. The resulting pyrrolidines had the following properties:

2-Methyl-5-n-propylpyrrolidine: b. p. 153-155° (755 mm); $n^{20}D$ 1.4413, d^{20}_4 0.8329. MR_D found 40.36. $C_8H_{17}N$. MR_D calculated 40.55.

2-Ethyl-5-n-propylpyrrolidine: b. p. 175-177° (760 mm); $n^{20}D$ 1.4463, d^{20}_4 0.8388. MR_D found 44.93. $C_9H_{19}N$. MR_D calculated 45.16.

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NITRO ESTERS OF C-SUBSTITUTED CARBOHYDRATES

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March, 1961
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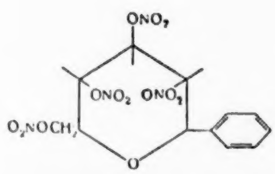
It is well known that nitro esters of polyhydroxy compounds are interesting in that certain of them have a vasodilating effect. Thus, for example, dianhydrosorbitol dinitrate is a very valuable medicinal compound which is used for the treatment of hypertension, angina pectoris, and other diseases of the cardiovascular system. For this reason, we have synthesized a number of nitro esters of carbon-substituted carbohydrates, which, in chemical structure, are anhydrides of substituted polyhydric alcohols.

Of the various methods for the synthesis of nitro esters of polyhydroxy compounds, we found it most convenient to use the reaction with concentrated nitric acid in acetic anhydride. This method has previously been proposed for sugars [1-4]. The nitro esters of glucopyranosyl-, galactopyranosyl-, rhamnopyranosyl-, xylopyranosyl-, and arabopyranosylbenzene were prepared. These compounds, which were prepared for the first time in the present work, were synthesized from the corresponding acetyl derivatives.

The majority of these nitro esters of C-substituted carbohydrates were snow-white crystalline substances, soluble in ether, benzene, the lower alcohols, acetone, chloroform, and ethyl acetate and insoluble in water and petroleum ether. They had a tendency to burn explosively.

EXPERIMENTAL

Glucopyranosylbenzene tetranitrate. To a solution of 3 g (0.125 mole) of glucopyranosylbenzene in 20 ml of acetic anhydride was added a solution of 6 ml of fuming nitric acid in 10 ml of acetic anhydride; the reaction mixture was cooled externally with ice during the addition. The mixture was warmed to room temperature and allowed to stand for 15 min. It was then poured into ice water and neutralized with potassium carbonate. The crude product amounted to 4.2 g. The substance was purified by treatment with an ether solution of anhydrous sodium sulfate containing activated carbon. The ether was distilled, and 2.14 g (41% of theoretical) of a snow-white crystalline prodcut with an m. p. of 102-104° was obtained. This material is described here for the first time. Its structure is represented by the formula



Found %: N 13.13, 13.00. $C_{12}H_{12}O_{13}N_4$. Calculated %: N 13.33.

Galactopyranosylbenzene tetranitrate. To a solution of 1.3 g (0.054 mole) of the previously described [5] galactopyranosylbenzene in 10 ml of acetic anhydride was added, with cooling, a solution of 3 ml of fuming nitric acid in 6 ml of acetic anhydride. Subsequent treatment was by the method described above. Distillation of the ether yielded 1.48 g of a transparent sirup. The sirup solidified on prolonged storage in a vacuum desiccator over phosphorus pentoxide. Recrystallization from isopropyl alcohol gave 0.6 g (26% of theoretical) of snow-white crystals with an m. p. of 108-110°. This material is described here for the first time.

Found %: N 13.57. $C_{12}H_{12}O_{13}N_4$. Calculated %: N 13.33.

Rhamnopyranosylbenzene tetranitrate. The rhamnopyranosylbenzene used in the synthesis has been described previously [6]. To 1.5 g (0.067 mole) of the material in 7 ml of acetic anhydride was added 4 ml of fuming nitric acid in 8 ml of acetic anhydride. Subsequent treatment was as described above. There was obtained 1.5 g (62.5% of theoretical) of a light-colored, transparent sirup, which we were unable to crystallize. The material is described here for the first time.

Found %: N 11.48. $C_{12}H_{13}O_{10}N_3$. Calculated %: N 11.69.

Xylopyranosylbenzene tetranitrate. The xylopyranosylbenzene used in the synthesis was previously prepared by us [5]. To a solution of 1 g (0.047 mole) of the substance in 7 ml of acetic anhydride was added dropwise a solution of 3 ml of fuming nitric acid in 4 ml of acetic anhydride. Subsequent treatment was as described above. There was obtained 1.45 g of a light-colored sirup, from which was obtained, by recrystallization from n-butyl and isopropyl alcohol, 0.9 g (55% of theoretical) of a white crystalline product with an m. p. 74-76°. The substance exploded when heated rapidly. This material is described here for the first time.

Found %: N 11.98. $C_{11}H_{11}O_{10}N_3$. Calculated %: N 12.17.

Arabopyranosylbenzene tetranitrate. Triacetyl-L-arabopyranosylbenzene, which we have described previously [7], was deacetylated with ammonia in absolute methanol. This yielded L-arabopyranosylbenzene in the form of a sirup; the substance has not previously been described.

To a solution of 2 g (0.094 mole) of arabopyranosylbenzene in 8 ml of acetic anhydride was carefully added, with cooling, 3 ml of fuming nitric acid in 7 ml of acetic anhydride. Subsequent treatment was as described above. After purification, there was obtained 1.9 g (58% of theoretical) of a snow-white crystalline product with an m. p. of 138-140°. The substance exploded when heated above the melting point. This material is described here for the first time.

Found %: N 11.79, 11.84. $C_{11}H_{11}O_{10}N_3$. Calculated %: N 12.17.

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CHARACTERISTICS OF THE ELECTROLYTIC DEPOSITION OF METALS FROM SOLUTIONS OF "EXTRAORDINARY" PURITY

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Investigations of reactions involving the evolution of hydrogen, which have been studied most completely [1-3], have shown that the rate of the electrode process can be appreciably influenced by contamination of the solution with even insignificant amounts of an impurity. Traces of contamination of either an organic or an inorganic origin have a significant effect on the electrolytic deposition of metals. However, too little attention up to now has been given to this problem.

Studies of the kinetics of the electrolytic deposition of metals have usually been made using so-called "chemically pure" salts which have been subjected to additional purification by recrystallization. However, this does not yield the purity required for such experiments; purification of the water from traces of organic contaminants is insufficient, and the presence of such impurities strongly affects the structure of the cathode deposits. Moreover, contact of the solutions investigated with various plastic materials with different "chemical stability" is frequently permitted, and this also affects the electrolytic crystallization process.

During the simultaneous discharge of metal and hydrogen ions (especially at low current densities in the case of such electronegative metals as zinc and manganese), traces of impurities change the current efficiency with respect to the metal and have an effect on cathode polarization and on the structure of the cathode deposit. With even the most insignificant contamination of the solution by organic impurities, it is impossible to establish the effect of small amounts of surface-active additives and of their structure and individual properties on the structure of the metal deposited at the cathode.

We present here our data on the electrolytic deposition of zinc and manganese from solutions of "extraordinary" purity.

Solutions of zinc sulfate were prepared from metallic zinc having a total impurity content of 10^{-5}% (prepared by the method of the Gipronikel Institute by distillation in a nitrogen atmosphere) and from distilled C. P. sulfuric acid and water, carefully freed from traces of organic impurities by prolonged boiling with potassium permanganate and triple distillation, the first portions (about 1/3) of the distillate being discarded. The resulting solution was additionally boiled and hydrolyzed with platinum electrodes.

Through the use of such a solution, containing "standard" [4] concentrations of zinc (60 g/liter) and sulfuric acid (100 g/liter), it was possible to deposit zinc at 20° with quite high current efficiencies—about 60% at low current densities of 1 amp/sq m and up to 99% at 5 amp/sq m — while when an electrolyte prepared from triply recrystallized C.P. zinc sulfate was used under the same conditions, considerable solution of the zinc was observed even at a current density of 30 amp/sq m.

The electrode potential of the high-purity zinc in a pure solution of zinc sulfate, both on open circuit and with a small current, was shifted 25-30 mv in a negative direction with respect to the potential of ordinary TsO grade electrolytic zinc.

During the work with high-purity solutions, it was necessary to give some attention to the material from which that portion of the cell in contact with the solution was constructed. Cathodic zinc deposits consisting of coarse, regular crystals with mirror-smooth faces were obtained only in glass apparatus.

When the cell was constructed from ordinary plastics (vinyl plastic, organic glass, polyethylene) and even from photographic film type plastic, there was a sharp change in the structure of the zinc deposit; the crystals became irregular, and their dimensions changed.

Figure 1 presents photomicrographs of the surface of cathodic zinc showing the sharp effect of the electrolytic cell material and of traces of organic impurities in the water on the structure of the deposit; this effect can be used as a specific and sensitive "indicator" of the purity of an electrolyte.

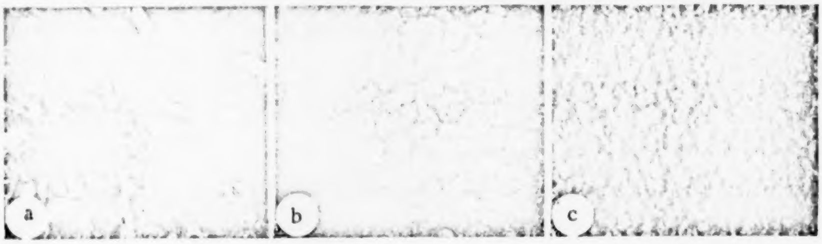

Fig. 1. Photomicrographs of cathodic zinc surfaces. Electrolyte: 35 g/liter of Zn, 150 g/liter of H_2SO_4; t = 50°; deposition time, 1 hr; D_c = 6000 a/m^2 · 40 ×. a) electrolytic cell and auxilliary apparatus constructed of glass; b) equipment for reinforcing electrode constructed from vinyl plastic; c) solution prepared from doubly distilled water without additional purification from traces of organic impurities.

The use of solutions of high purity for the electrolytic deposition of zinc has permitted us to develop a method of high reproducibility for the measurement of the active surface of zinc [5]. This method can be used in investigations of the surface of other pure metals.

No less interesting results were obtained during the electrolytic deposition of manganese from pure solutions. The electrolyte, which consisted of 50 g /liter of manganese in the form of the chloride and 110 g/liter of ammonium chloride, was prepared from electrolytic metal, distilled C.P. hydrochloric acid, and gaseous ammonia in doubly distilled water which had been boiled with permanganate. Only the central thirds of the acid and water distillates were used. Solution of the manganese was carried out at a low concentration (pH > 1). The solution was subjected to sulfide purification with manganese sulfide prepared from a previously purified solution of manganese chloride and ammonium sulfide; the latter was prepared by absorption of hydrogen sulfide in a solution of ammonia in doubly distilled water. The hydrogen sulfide was prepared from C.P. sodium sulfide and was freed from arsenic.

After sulfide purification, the manganese electrolyte was electrolyzed at a low overall current density of 20-50 a/m^2 in a glass cell containing a glass anode compartment with a glass diaphragm, a platinum anode, and a cathode of pure aluminum. The catholyte was continuously stirred with a stirrer, and the anode gases were removed by suction. Manganese hydroxide was precipitated in the catholyte, and this was further oxidized by atmospheric oxygen to manganese dioxide, which adsorbed possible organic and inorganic impurities from the electrolyte. After filtration, the solution was again electrolyzed; this operation was repeated three times. After treatment of the solution by electrolysis, which was carried out for a total time of 200-220 hr, to the solution was added aluminum hydroxide prepared by anodic solution of manganese chloride at a current density of 10 a/m^2, and, finally, the solution was filtered through a glass filter.

Manganese was successfully deposited electrolytically at a current density of only 10 a/m^2 from a solution of the indicated purity at a pH of 7 at a temperature of 20°. At higher current densities, it was possible to obtain cathodic manganese at high, previously unobtainable current efficiencies:

Current density, a/m^2:	400	660	1000	2000
Electrolysis time, hours	6^{52}	4^{08}	2^{45}	1^{23}
Current efficiency, %	84	93	91	90

All of the cathodic manganese deposits had a clearly crystalline structure (see Fig. 2), even when particles of manganese hydroxides were suspended in the catholyte. That others have obtained cathodic manganese deposits of the so-called vaguely crystalline type [6] and the impossibility of precipitating manganese at low current densities [7] are caused, in our opinion, by impurities in the electrolyte.

We have thus established that the process of the formation and growth of crystals of the electronegative metals zinc and manganese in pure electrolytes does not differ in principle from the electrolytic crystallization of silver

described by A. T. Vagramyan [8], and we feel that the kinetics of electrolytic crystallization and the effect of additives should be studied in especially pure electrolytes.

Fig. 2. Photomicrographs of the surface of cathodic manganese. Electrolyte: 50 g/liter of Mn, 110 g/liter NH_4Cl; t = 20°; amount of electricity, 0.275 amp-hours/cm^2. 40 ×. a) D_c = 50 a/m^2; b) D_c = 400 a/m^2.

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ORGANOSILICON MONOMERS WITH FLUORINE-CONTAINING CYCLOBUTANE RINGS

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According to the literature [1-3], organosilicon polymers containing fluorinated cyclobutane rings have a number of valuable properties. The method of synthesis of the monomers from which these polymers are prepared includes the condensation of tetrafluoro- and trifluorochloroethylenes with alkenylsilanes; the reaction takes place under pressure and requires 24-36 hr [1-4]. The reaction takes place according to:

$$CF_2=CFCl + CH_2=CHSiCl_3 \xrightarrow[24\text{ hours}]{210°} Cl_3Si\overline{CHCFClCF_2CH_2};$$

$$CF_2=CF_2 + CH_2=CHSi(CH_3)Cl_2 \xrightarrow[36\text{ hours}]{210°} CH_3(Cl_2)Si\overline{CHCF_2CF_2CH_2}\ \text{etc.}$$

Another route for the synthesis of organosilicon monomers containing fluorinated cyclobutane rings was studied in the present work; the route is described by the equations:

$$CH_2=CH-CH=CH_2 + CF_2=CF_2 \rightarrow CH_2=CH\overline{CHCF_2CF_2CH_2};$$

$$R_nCl_{3-n}SiH + CH_2=CH\overline{CHCF_2CF_2CH_2} \xrightarrow{H_2PtCl_6} R_nCl_{3-n}SiCH_2CH_2\overline{CHCF_2CF_2CH_2};$$

$$R=CH_3,\ C_2H_5,\ C_6H_5;\ n=0,\ 1,\ 2,\ 3.$$

The condensation of butadiene with tetrafluoroethylene (scheme 1) takes place fairly readily. The yield of $CH_2=CH\overline{CHCF_2CF_2CH_2}$ by this reaction reaches 90% [5]. An examination of Table 1 shows that all of the silanes used added to vinyltetrafluorocyclobutane in the presence of chloroplatinic acid giving high yields of the reaction

Expt. No.	Silane	Amt., g (mole)	Vinyltetra-fluorocyclo-butane, g(mole)	Amt. 0.1 M soln. H_2PtCl_6, ml	Wt. reaction product	Reaction product	Yield	
							g	%
1	Cl_3SiH	13.6 (0.1)	15.4 (0.1)	0.1	27.5	$Cl_3SiCH_2CH_2\overline{CHCF_2CF_2CH_2}$	26.5	91.0
2	CH_3SiCl_2H	14.0 (0.12)	16.5 (0.11)	0.2	29.5	$CH_3(Cl_2)SiCH_2CH_2\overline{CHCF_2CF_2CH_2}$	25.8	91.0
3	$C_2H_5SiCl_2H$	8.0 (0.06)	9.0 (0.06)	0.1	16.0	$C_2H_5(Cl_2)SiCH_2CH_2\overline{CHCF_2CF_2CH_2}$	13.9	82.0
4	$CH_3(C_2H_5)SiClH$	10.9 (0.1)	15.4 (0.1)	0.1	25.7	$CH_3(C_2H_5)(Cl)SiCH_2CH_2\overline{CHCF_2CF_2CH_2}$	20.6	79.0
5	$CH_3(C_2H_5)_2SiH$	10.5 (0.1)	15.4 (0.1)	0.1	24.5	$CH_3(C_2H_5)_2SiCH_2CH_2\overline{CHCF_2CF_2CH_2}$	18.3	72.0
6	$C_6H_5SiCl_2H$	6.8 (0.04)	6.0 (0.04)	0.05	11.3	$C_6H_5(Cl_2)SiCH_2CH_2\overline{CHCF_2CF_2CH_2}$	8.9	70.0
7	Cl_2SiH_2	7.5 (0.075)	23.2 (0.15)	0.3	25.6	$Cl_2Si(CH_2CH_2\overline{CHCF_2CF_2CH_2})_2$	14.2	46.0

products. Through the use of relatively more vigorous conditions (in an autoclave at 130°) in the presence of chloroplatinic acid, we were able to add dichlorosilane to two molecules of vinyltetrafluorocyclobutane, thereby obtaining the corresponding monomer in 46% yield, as may be seen from Table 1.

EXPERIMENTAL

1. β-(2,2,3,3-Tetrafluorocyclobutylethyl)trichlorosilane $Cl_3SiCH_2CH_2CHCF_2CF_2CH_2$. In a 250 ml three-neck round-bottom flask fitted with a mechanical stirrer, a reflux condenser and a dropping funnel was placed 4 ml of vinyltetrafluorocyclobutane, 0.1 ml of an 0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol, and 1 ml of $HSiCl_3$. The reaction mixture was heated on a water bath until the reaction began (about 80°), and then a mixture of $CH_2 = CHCHCF_2CF_2CH_2$ and $HSiCl_3$ [total amount charged: 15.4 g (0.1 mole)] $CH_2 = CHCHCF_2CF_2CH_2$ and 13.6 g (0.1 mole) of $HSiCl_3$) was gradually added. The addition was made at a rate such that the temperature was maintained at the level indicated above. When the addition of the reagents was complete, the reaction mixture was heated for an additional 15 min on the water bath with vigorous stirring. The crude mixture of reaction products (27.5 g) was distilled under vacuum, and 26.5 g (91%) of $Cl_3SiCH_2CH_2CHCF_2CF_2CH_2$ was obtained; b. p. 103.5-104.0° (31 mm); d^{20}_4 1.4395, $n^{20}D$ 1.4160; found MR_D 50.48; calculated 50.31.

Found %: C 25.11, 25.21; H 2.89, 3.02; Cl 36.56, 36.50. $C_6H_7SiCl_3F_4$. Calculated %: C 24.89; H 2.44; Cl 36.76.

2. β-(2,2,3,3-Tetrafluorocyclobutylethyl)methyldichlorosilane $CH_3(Cl_2)SiCH_2CH_2CHCF_2CF_2CH_2$. The reaction was carried out under the conditions described for experiment 1. Vacuum distillation of 29.5 g of crude reaction product gave 25.8 g (91%) of $CH_3(Cl_2)SiCH_2CH_2CHCF_2CF_2CH_2$ with a b. p. of 105-105.5° (28.5 mm); d^{20}_4 1.3151; $n^{20}D$ 1.4120; found MR_D 50.93; calculated 50.68.

Found %: C 31.38, 31.45; H 3.94, 3.86; Cl 26.07, 26.06. $C_7H_{10}SiCl_2F_4$. Calculated %: C 31.30; H 3.72; Cl 26.05.

3. β-(2,2,3,3-Tetrafluorocyclobutylethyl)ethyldichlorosilane $C_2H_5(Cl_2)SiCH_2CH_2CHCF_2CF_2CH_2$. The reaction was carried out under the conditions described for experiment 1. Vacuum distillation of 16 g of crude reaction product gave 13.9 g (82%) of $C_2H_5(Cl_2)SiCH_2CH_2CHCF_2CF_2CH_2$ with a b. p. of 99° (11 mm); d^{20}_4 1.2834, $n^{20}D$ 1.4180; found MR_D 55.61; calculated 55.19.

Found %: C 34.54, 34.44; H 4.79, 4.69; Cl 24.87, 24.68. $C_8H_{12}SiCl_2F_4$. Calculated %: C 33.92; H 4.26; Cl 25.00.

4. β-(2,2,3,3-Tetrafluorocyclobutylethyl)methylchlorosilane $CH_3(C_2H_5)(Cl)SiCH_2CH_2CHCF_2CF_2CH_2$. The reaction was carried out under the conditions described for experiment 1. Vacuum distillation of 25.7 g of the crude reaction product gave 20.6 g (79%) of $CH_3(C_2H_5)(Cl)SiCH_2CH_2CHCF_2CF_2CH_2$ with a b. p. of 96-96.5° (13.5 mm), d^{20}_4 1.1663, $n^{20}D$ 1.4102; found MR_D 55.84; calculated 55.56.

Found %: C 41.03, 41.05; H 5.68, 5.81; Cl 13.33, 12.79. $C_9H_{15}SiClF_4$. Calculated %: C 41.10; H 5.75; Cl 13.47.

5. β-(2,2,3,3-Tetrafluorocyclobutylethyl)methyldiethylsilane $CH_3(C_2H_5)_2SiCH_2CH_2CHCF_2CF_2CH_2$. The reaction was carried out under the conditions described for experiment 1. Vacuum distillation of 24.5 g of the crude reaction product gave 18.3 g (72%) of $CH_3(C_2H_5)_2SiCH_2CH_2CHCF_2CF_2CH_2$ with a b. p. of 86-86.5° (11 mm), d^{20}_4 1.0373, $n^{20}D$ 1.4070; found MR_D 60.84; calculated 60.94.

Found %: C 52.01, 52.24; H 7.92, 7.79; F 29.69, 29.69. $C_{11}H_{20}SiF_4$. Calculated %: C 51.79; H 7.83; F 29.66.

6. β-(2,2,3,3-Tetrafluorocyclobutylethyl)phenyldichlorosilane $C_6H_5(Cl_2)SiCH_2CH_2CHCF_2CF_2CH_2$. The reaction was carried out under the conditions described for experiment 1. Vacuum distillation of 11.3 g of the crude reaction product gave 8.9 g (70%) of $C_6H_5(Cl_2)SiCH_2CH_2CHCF_2CF_2CH_2$ with a b. p. of 119.5-120° (3.5 mm), d^{20}_4 1.3223, $n^{20}D$ 1.4836; found MR_D 70.90; calculated 70.35.

Found %: C 44.55, 44.27; H 3.69, 3.92; Cl 21.90, 21.68. $C_{12}H_{12}SiCl_2F_4$. Calculated %: C 43.80; H 3.64; Cl 21.26.

7. Bis(β-2,2,3,3-tetrafluorocyclobutylethyl)dichlorosilane $Cl_2Si(CH_2CH_2\overline{CHCF_2CF_2CH_2})_2$. A mixture of 23.2 g (0.15 mole) of $CH_2 = CH\overline{CHCF_2CF_2CH_2}$, 7.5 g (0.075 mole) of H_2SiCl_2, and 0.3 ml of an 0.1 M solution of $H_2PtCl_2 \cdot 6H_2O$ in isopropyl alcohol was placed in a glass test tube, and the tube was placed in a 200 ml stainless still autoclave. The mixture was heated to a temperature of 120°, where there was a sharp jump in the temperature to 158°. The pressure remained constant at 5.5 atm. The reaction time was 2 hr. The residual pressure was 1 atm when the autoclave was discharged. Vacuum distillation of 25.6 g of the crude reaction product gave 14.2 g (46%) of crystalline $Cl_2Si(CH_2CH_2\overline{CHCF_2CF_2CH_2})_2$ with a b. p. of 125-126° (2.5 mm).

Found %: C 35.17, 35.55; H 3.48, 3.57; Cl 17.10, 17.35. $C_{12}H_{14}SiCl_2F_8$. Calculated %: C 35.18; H 3.48; Cl 17.32.

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REARRANGEMENT DURING HOMOLYTIC ADDITION OF HYDROGEN BROMIDE TO POLYHALOALKENES

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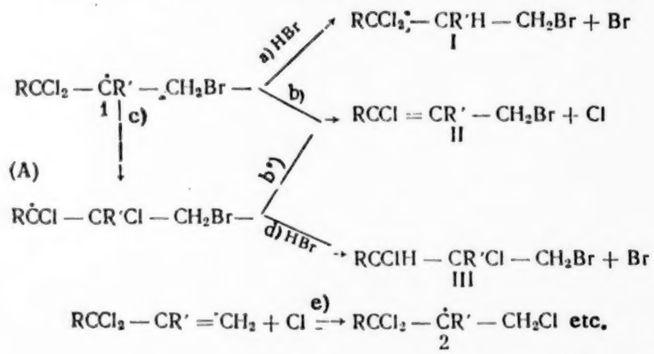
It has previously been found [1-5] that radicals of the type $CCl_3\dot{C}X-CH_2Y$, where X = H, Cl, Br, CH_3 and Y = Cl, Vr, CCl_3, or SC_6H_5, isomerize into radicals having the structure $\dot{C}Cl_2-CXCl-CH_2Y$. We have noted a similar rearrangement [6] in the case of a radical with a dichloromethyl group, $CHCl_2-\dot{C}H-CH_2Br$, which isomerizes to the more stable radical $CHCl-CHCl-CH_2Br$.

The ability of radicals of the structure $RCCl_2\dot{C}R'CH_2Br$ (R = H, CH_3; R' = H, CH_3), which contain a dichloromethyl or a dichloromethylene group alpha to the radical center, to undergo such a rearrangement was investigated in the present work; the radicals were generated during the homolytic addition of hydrogen bromide to the corresponding unsaturated compound $RCCl_2CR' = CH_2$

$$RCl_2-CR'=CH_2 \xrightarrow[(C_6H_5CO_2)_2]{HBr} RCCl_2-\underset{1}{\dot{C}R'}-CH_2Br.$$

It might well be expected that in the reactions studied, radical 1 would react in accordance with scheme A:



where R and R' = H or CH_3; radical 2 undergoes the same reaction as radical 1.

In the present case, it was interesting to compare the stability of the original radicals with that of the radicals which could be formed by rearrangement, namely: The stability of the secondary radical $CH_3CCl_2-\dot{C}H-CH_2Br$ with that of the formally secondary radical $CH_3\dot{C}Cl-CHCl-CH_2Br$ which has a chlorine rather than a hydrogen attached to the radical center $CHCl_2-\dot{C}R'-CH_2Br$, and the stability of the secondary and tertiary radicals (R' = H or CH_3) with that of the primary radical having a chlorine attached to the carbon bearing the free electron, $\dot{C}HCl-CClR'-CH_2Br$.

The addition of hydrogen bromide to 3,3-dichloro-1-butene leads to the formation of only one rearranged reaction product, 2,3-dichloro-1-bromobutane (see scheme A, course c, d; R = CH_3; R' = H).

We have previously shown that the interaction of hydrogen bromide with 1,1-dichloro-2-propene takes place with the formation of the rearrangement product 1,2-dichloro-3-bromopropane. By carrying out the experiment in a solvent and by working with a large amount of material, we were able, in the present work, to separate the unrearranged reaction product, 1,1-dichloro-3-bromopropane (see scheme A, course a, c, d; R and R' = H), in addition to 1,2-dichloro-3-bromopropane.

Olefin	Total yield of HBr addition products, % of theoretical	Rearrangement, %
$CH_3CCl_2-CH=CH_2$	73	100
$CHCl_2-CH=CH_2$	53	90
$CHCl_2-C(CH_3)=CH_2$	61	50-55
$CHCl_2-CCl=CH_2$	22	0

1,1-Dichloro-2-methyl-2-propene reacts with hydrogen bromide with the formation of a mixture of reaction products consisting of the rearranged 1,2-dichloro-3-bromo-2-methylpropane (III), the rearranged 1,1-dichloro-3-bromo-2-methylpropane (I), trichloroisobutane, and 1-chloro-3-bromo-2-methyl-1-propene (II). The formation of these substances can be represented by a scheme analogous to scheme A (R = H, R' = CH_3).

In order to exclude the possibility that the rearranged reaction products were formed by allyl isomerization of the original unsaturated compounds with subsequent addition of hydrogen bromide to yield the structures $CH_3CHCl-CHBr-CH_2Cl$ and $CH_2Cl-C(CH_3)Br-CH_2Cl$, respectively, control experiments were carried out in which hydrogen bromide was added to $CH_3CCl=CH-CH_2Cl$ and $CHCl=C(CH_3)-CH_2Cl$ (allylic isomers of the original unsaturated compounds) in the presence of benzoyl peroxide; these experiments gave negative results.

The yield of addition products and the dependence of the amount of rearrangement on the structure of the original olefin are shown in Table 1.

On the basis of these data, the radicals studied can be arranged in the following order with respect to stability: $CHCl_2-\dot{C}ClCH_2Br > \dot{C}HClCCl_2CH_2Br$; $CH_3\dot{C}ClCHClCH_2Br > CH_3CCl_2\dot{C}HCH_2Br$; $\dot{C}HClCHClCH_2Br > CHCl_2\dot{C}HCH_2Br$; $CHCl_2\dot{C}(CH_3)CH_2Br \approx \dot{C}HClCCl(CH_3)CH_2Br$.

EXPERIMENTAL

Addition of hydrogen bromide to $CH_3CCl_2-CH=CH_2$. A solution of 16 g of $CH_3CCl_2CH=CH_2$* and 0.5 g of benzoyl peroxide in 48 g of carbon tetrachloride was saturated with hydrogen bromide at 70-75°. The reaction mixture was washed with a solution of sodium carbonate and with water and dried over $CaCl_2$, and distillation of the solvent then yielded 18.5 g (73% of theoretical) of 2,3-dichloro-1-bromobutane with a b. p. of 67-67.5° at 12 mm, $n^{20}D$ 1.5042, d^{20}_4 1.5985; found MR 38.15; calculated 38.17.

Found %: C 23.06, 23.30; H 3.52, 3.32. $C_4H_7Cl_2Br$. Calculated %: C 23.33; H 3.43.

The picrate of $CH_3CHCl-CHCl-CH_2S-C=NH(NH_2)$, melted at 165-165.6° (from alcohol).

Found %: C 30.91, 31.09; H 3.23, 3.28; N 16.80, 16.76. $C_{11}H_{13}Cl_2N_5O_7S$. Calculated %: C 30.71; H 3.05; N 16.28.

Dehydrobromination of 13.6 g of $CH_3CHClCHClCH_2Br$ with 4.1 g of KOH in Ethyl Cellosolve gave 4.1 g (60% of theoretical) of 2,3-dichloro-1-butene with a b. p. of 11-112°, $n^{20}D$ 1.4580, d^{20}_4 1.1340 (literature values: b. p. 111.8°, $n^{20}D$ 1.4571, d^{20}_4 1.1411 [7]). Ozonolysis of $CH_3CHClCCl=CH_2$ yielded formaldehyde, the dimedone derivative of which melted at 185-186° (literature value [8]: 188-189°), and α-chloropropionic acid,** which was identified in the form of its anilide which melted at 88° (literature value [9]: m. p. 92°).

Found %: C 58.72, 58.53; H 5.44, 5.46; Cl 20.20, 20.06. $C_9H_{10}ClNO$. Calculated %: C 58.83; H 5.49; Cl 19.31.

Addition of HBr to $CHCl_2CH=CH_2$. A solution of 143 g of $CHCl_2CH=CH_2$ and 1.5 g of benzoyl peroxide in 240 g of heptane was saturated with hydrogen bromide at 80°. After the treatment described for the preceding experiment and distillation in a column at 34 mm, 131 g of a mixture of dichlorobromopropanes (53% of theoretical) was obtained. Three fractions were obtained: I, b. p. 71-77°, $n^{20}D$ 1.5034 – 1.5080, 12 g (9% of the total product); II, b. p. 81°, $n^{20}D$ 1.5170, d^{20}_4 1.7504, 113.7 g (86% of the total product).

* Constants of $CH_3CCl_2CH=CH_2$: b. p. 95°, $n^{20}D$ 1.4460, d^{20}_4 1.1043.

** The α-chloropropionic acid was obtained from the ozonolysis products without additional oxidation.

Distillation of fraction I gave 1,1-dichloro-3-bromopropane with a b. p. of 74-74.5° at 34 mm , $n^{20}D$ 1.5045, d^{20}_4 1.7084; found MR 33.39, calculated 33.55.*

The picrate of $CHCl_2CH_2-CH_2S-C=NH(NH_2)$ melted at 147-148° (from alcohol).

Found %: C 28.82, 28.56; H 2.56, 2.62. $C_{10}H_{11}Cl_2N_5O_7S$. Calculated %: C 28.86; H 2.67.

A mixture of this picrate with the picrate obtained from known $CHCl_2-CH_2-CH_2Br$ melted at 147-148°; a mixture with the picrate of $CH_2Cl-CHCl-CH_2S-C=NH(NH_2)$ melted at 139°. See reference [6] for the structure of the substance forming fraction II.

Addition of hydrogen bromide to $CHCl_2C(CH_3)=CH_2$. A solution of 45 g of $CHCl_2C(CH_3)=CH_2$ and 0.5 g of benzoyl peroxide in 110 g of carbon tetrachloride was saturated with hydrogen bromide at 80° until the index of refraction ceased to change. After the usual treatment, distillation of the reaction products in a column at 17 mm yielded the following fractions: I 52-60°, $n^{20}D$ 1.4929, 7.4 g; II 60-66°, $n^{20}D$ 1.4886, 2.7 g; III 69.5-71°, $n^{20}D$ 1.5025, d^{20}_4 1.6098; found MR 37.38; calculated for $C_4H_7Cl_2Br$ 38.17; 46.2 g (61% of theoretical).

Fractions I and II contained a mixture of $CHCl=C(CH_3)-CH_2Br$ and trichloroisobutane. The first fraction was resolved by treatment with thiourea under mild conditions; this gave $CHCl=C(CH_3)-CH_2S-C=NH(NH_2)$, the picrate of which melted at 193° (from alcohol). A mixture of this material with a known sample melted without depression of the melting point.

Found %: C 33.58, 33.86; H 3.17, 3.20; N 17.37, 17.38. $C_{11}H_{12}ClN_5O_7S$. Calculated %: C 33.55; H 3.07; N 17.78.

Distillation of the remaining material yielded trichloroisobutane with a b. p. of 160°, $n^{20}D$ 1.4765, d^{20}_4 1.2918; found MR 35.29, calculated 35.27. (Constants of 1,2,3-trichloro-2-methylpropane prepared by an independent route [10] were: b. p. 163°, $n^{20}D$ 1.4770, d^{20}_4 1.3010).

Fraction III was a mixture of 3,3-dichloro-1-bromo-2-methylpropane and 2,3-dichloro-1-bromo-2-methylpropane.

Found %: C 23.27, 23.43; H 3.33, 3.28. $C_4H_7Cl_2Br$. Calculated %: C 23.33; H 3.43.

Heating of 8.4 g of the mixture (fraction III) with 3.1 g of thiourea, in alcohol, in a sealed tube for 20 hr followed by the appropriate treatment yielded: 1) 6.4 g of a dry residue consisting of unreacted thiourea and the isothiourea derivative of $CHCl_2C(CH_3)H-CH_2SC=NH(NH_2)$ (yield, 40% of theoretical); m. p. of picrate 164-165° (from alcohol).

Found %: C 31.01, 30.90; H 3.07, 3.15; N 15.84, 15.95. $C_{11}H_{12}Cl_2N_5O_7S$. Calculated %: C 30.71; H 3.05; N 16.24.

2) An oil, 3.6 g (42% of theoretical) from which was separated by distillation 1,2-dichloro-3-bromo-2-methylpropane with a b. p. of 67-68° at 16 mm, $n^{20}D$ 1.5040, d^{20}_4 1.6154; Found MR 37.71, calculated 38.18.**

Dehydrobromination of 45 g of the dichlorobromoisobutane fraction with 15 g of KOH in Ethyl Cellosolve at 0° gave: 1) 8.5 g of $CHCl_2-C(CH_3)=CH_2$ with a b. p. of 49-50° at 105 mm, $n^{20}D$ 1.4560, d^{20}_4 .1346 (constants of $CHCl_2C(CH_3)=CH_2$ prepared by the method of reference [11] were: b. p. 48-49° at 100 mm, $n^{20}D$ 1.4582, d^{20}_4 1.1344.

Ozonolysis of $CHCl_2-C(CH_3)=CH_2$ gave formaldehyde, which was identified in the form of its dimedone derivative.

* $CHCl_2-CH_2-CH_2Br$ prepared by an independent route had the following constants: b. p. 72° at 30 mm, $n^{20}D$ 1.5030, d^{20}_4 1.7093, found MR 33.19.

Found %: C 18.88, 18.91; H 2.58, 2.53. $C_4H_7Cl_2Br$. Calculated %: C 18.77; H 2.63.

** 1,2-Dichloro-3-bromo-2-methylpropane prepared by chlorination of $CH_2=C(CH_3)-CH_2Br$ in an acid medium, had the following constants: b. p. 75° at 21 mm, $n^{20}D$ 1.5071, d^{20}_4 1.6110.

Found %: C 23.50, 23.62; H 3.47, 3.57. $C_4H_7Cl_2Br$. Calculated %: C 23.33; H 3.43.

2) Unreacted 1,2-dichloro-3-bromo-2-methylpropane, 20.4 g, with a b. p. of 112-113° at 100 mm, $n^{20}D$ 1.5038, d^{20}_4 1.6124; found MR 37.75, calculated 38.18. This substance did not react with thiourea even under vigorous conditions. Treatment of the compound with Zn in alcohol gave $CH_2Cl-C(CH_3)=CH_2$, which was identified in the form of the picrate of the isothiourea derivative, m. p. 168-169°.

The analogous isothiourea derivative was prepared from a known sample of $CH_2Cl-C(CH_3)Cl-CH_2Br$ by the same method (reaction with Zn followed by reaction with thiourea); the picrate of this derivative melted at 168-169.5° (from alcohol)

Found %: C 36.42, 36.59; H 3.63, 3.44; N 20.01, 20.23. $C_{11}H_{13}N_5O_7S$. Calculated %: C 36.76; H 3.66; N 19.49.

A mixture of the two picrates melted at 168-169°.

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A STUDY OF BICYCLIC TERPENES AND THEIR OXIDES BY THE PROTON MAGNETIC RESONANCE TECHNIQUE

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There exists in the literature only isolated data on the PMR spectra for bicyclic terpenes. Such are the data on the PMR of camphor, α-chloro-, α-bromo-, and αα'-dibromocamphor [1], and of camphene [2]. There exist some references to the frequencies of some PMR lines for α and β pinenes [3] and for pinocamphone [4]. We could find no data on the PMR spectra of oxides of bicyclic terpenes. In the present work the PMR spectra of DΔ^3-carene, DΔ^3-carene oxide, Dα-pinene, Lα-pinene, DLα-pinene, the D-oxide of α-pinene, the L-oxide of α-pinene, β-pinene, the oxide of β-pinene, semicyclic carenol, and DL-trans-pinocarveol are investigated.

The spectra were obtained on a permanent magnet NMR spectrometer at v = 24.458 mc/sec (H_0 = 5730 oe). The spectrographic data were processed by Yu. Yu. Samitov, the limiting relative resolving power of the gap was equal to $5 \cdot 10^{-8}$, and benzene was employed as the internal standard; the diameter of the cylindrical ampoules was 3.0 mm with a sample volume of about 0.1 cm^3, the position of the lines was determined by the "side band" technique with an accuracy of ± 1 c/sec and was checked by interpolation from two standards with a relative accuracy of $\pm 0.4 \cdot 10^{-7}$. The spectra were photographed directly from the screen of an ÉNO-1 oscillograph, the curvature of the screen being allowed for, and the field sweep rate was equal to 0.5 millioersted/sec.

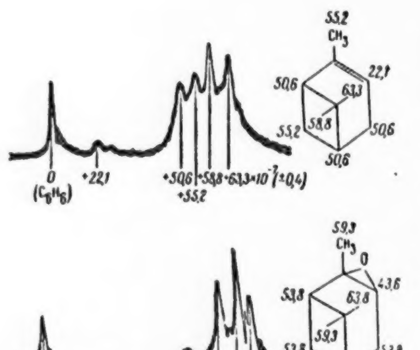


Fig. 1.

The spectrum of Dα-pinene is given in Fig. 1. The spectra of Lα-pinene and DLα-pinene proved, as expected, to be identical with the spectrum of Dα-pinene. There are five peaks in the spectrum with the following chemical shifts referred to benzene, expressed in units of 10^{-7} (ten millionths of the applied field): 22.1 (1); 50.6 (4); 55.2 (5); 58.8 (3) and 63.3 (3). The approximate integral relative peak intensities, the numerical values of which should theoretically correspond to the number of protons in the molecule contributing to the given line, are indicated in brackets. The chemical shift of 22.1 should be assigned to a proton at a double bond; this value agrees with published data for a proton at a C=C bond. There is a reference in Conroy's review [4] to a value of the chemical shift for the methyl group at the double bond in α-pinene, equal to τ = 8.37, which agrees closely with the value of 55.2 obtained by us (we calculated that the position of the benzene peak on the τ-scale was defined by a value of 2.84 [4]). The chemical shifts of 58.8 and 63.3 correspond to the two methyl radicals of the gem-dimethyl group. The large value of the shift for one of these methyl radicals (63.3) and the large difference (4.5 units) between the values of the shifts of the two methyl groups merit attention. This phenomenon will be considered later. It is somewhat more difficult with the given resolution of the spectrum to identify the chemical shifts for the methylene groups and the protons of the picean group. In our opinion the line with the value of 50.6 is due to the protons of the methylene group next to the double bond and the protons of the picean group, while the protons of the other methylene group contribute to the line with a chemical shift of 55.2. The spectrum of the L-oxide of α-pinene (the spectrum of the D-oxide and of α-pinene is identical with the spectrum of the L-oxide) having the following chemical shift: 43.6 (1); 53.8 (6); 59.3 (6); 63.8 (3) is given in Fig. 1.

Comparison of the spectrum of pinene oxide with that of α-pinene reveals the disappearance of the line with a shift equal to 22.1, which corresponds to a proton at a C=C bond, and the appearance of a peak with a value of 43.6 corresponding to a proton at an oxide ring (for $-CH\overset{O}{\frown}C\langle^{CH}$ in furmagilin the values τ = 7.20-7.65 or, with reference to benzene, 43.6-48.1 are given [2]). It should be pointed out that the chemical shift for the methyl at the epoxide ring in the spectrum of the oxide of α-pinene is equal to 59.3, i.e., close to the value of 60.6 given for the methyl radical at the epoxide ring in furmagalin [2], and that two peaks with high chemical shift values for the gem-dimethyl groups are retained and the shift for the methyl group at the oxide ring is increased.

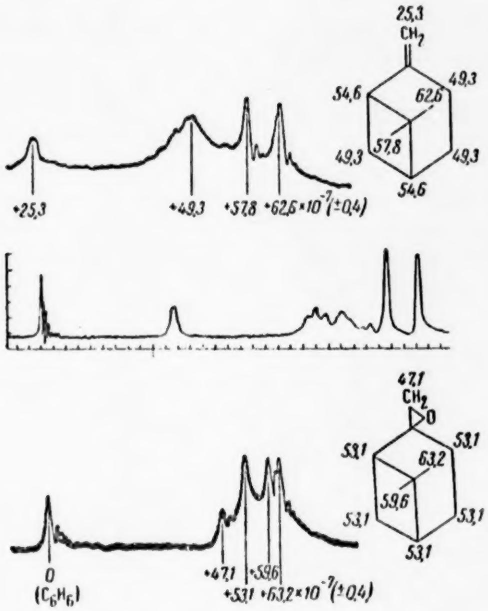


Fig. 2.

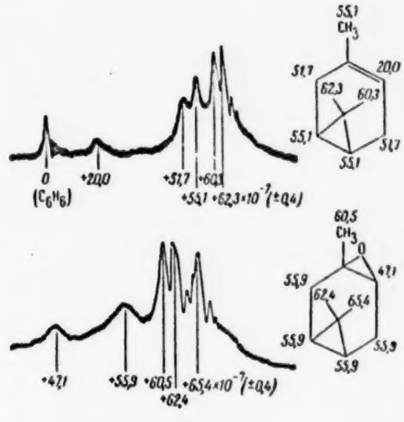


Fig. 3.

The PMR spectrum for β-pinene is presented in Fig. 2a. Four main peaks with values of 25.3 (2); 49.3 (8); 57.8 (3); 62.6 (3) can be distinguished in the spectrum. It can be seen from the spectrum that the peak at 49.4 is poorly resolved. In it a peak with a chemical shift of 54.6 (2) may be discerned. The shift of 25.3 can be related to the protons of the methylene group of the semicyclic bond (the values 24.0 and 27.5 are given for camphene [2]). The lines with shifts 62.9 and 57.9 are linked with the gem-dimethyl group. The spectrum of β-pinene obtained on a high resolution spectrograph (Japan Nuclear Magnetic Spectrometer) confirmed the supposition that the peak with a value of 49.3 is complex, which can be seen from the spectrum presented in Fig. 2b. We did not assign the chemical shifts in the range 44-54 to any definite protons in the β-pinene molecule.

The spectrum of the oxide of β-pinene is given in Fig. 2c. The values of the chemical shifts and their intensities are characterized by the following data: 47.1 (2); 53.1 (8); 59.6 (3) and 63.2 (3), and a poorly resolved peak in the region of 50 (1) can also be discerned. The spectrum of the oxide of β-pinene is similar to the spectrum of α-pinene with the exception of the lines due to the protons at the epoxide ring. In the oxide of β-pinene these protons give lines with higher values for the shifts, which agrees with literature data on the chemical shift for the $CH_2\overset{O}{\frown}C$ grouping (the chemical shift for isobutylene is equal to 46 [2]). The chemical shifts of 63.2 and 59.6 should be assigned to the methyl radicals of the gem-dimethyl group. The poorly resolved peak corresponds to the six protons of the methylene groups and the two protons of the picean group.

The spectrum of DΔ^3-carene which has five peaks: 20.0 (1); 51.8 (4); 55.1 (5); 60.3 (3); 62.3 (3) is presented in Fig. 3. Resonance at 20.0 is due to the proton at the double bond. The position of the peak due to the protons of the methyl group at the double bond, equal to 55.1, is close in value to the analogous methyl group in α-pinene (55.2). The peaks at 62.3 and 60.3 correspond to gem-dimethyl radicals. The methylene groups should clearly be represented by values of 51.8. It is not altogether clear to which line the CH groups of the cyclopropane ring

contributed. In a preliminary report on the structure of cycloheptatriene derivatives Corey, Burke and Remers [7] give the PMR spectrum for Δ^2-4-methylcarene-2-one in which the 54.8 line is assigned to the protons of the cyclopropane ring. Therefore in the case of Δ^3-carene the peak at 55.1 to which the protons of the $CH_3-C=$ group also contribute may be assigned to the protons of the cyclopropane group. The PMR spectrum data for bicyclic terpenes and their oxides showed that the presence of an epoxide ring is clearly demonstrated by the PMR method [3].

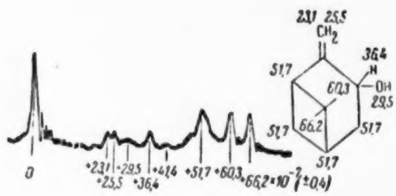
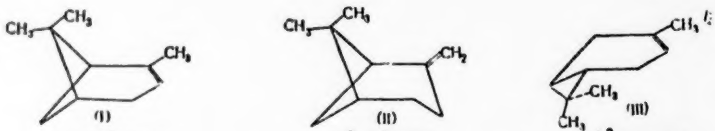


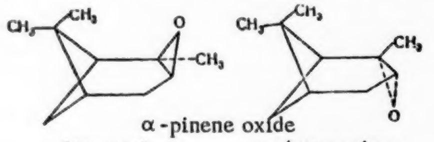
Fig. 4.

Analysis of the PMR spectra of bicyclic terpenes and their oxides also enables some conclusions to be drawn regarding their conformation. The high values of the shifts for the methyl groups of the gem-dimethyl groupings in bicyclic terpenes and the different values of the shifts for each of these groups indicate the existence of a diamagnetic shift undergone by one of the gem-dimethyl groups. The reason for this is the magnetic anisotropy of the double bond. A group located in a cone-shaped zone above or below the plane of the bond undergoes a diamagnetic shift (the line is displaced in the direction of high field strengths). Thus in the case of α- and β-pinene only one of the gem-dimethyl groups undergoes a diamagnetic shift (of the order of 2-3 tenthousandths of the applied field [3]). A displacement of this kind is in good agreement with the conformation of α- and β-pinene [9] (see formulas I and II). As regards Δ^3-carene, no precise data on its conformation are available. The significant difference in the chemical shifts of the gem-dimethyl groups (two units) indicates the existence of diamagnetic screening by the double bond at one of them in the case of DΔ^3-carene as well (see formula III).



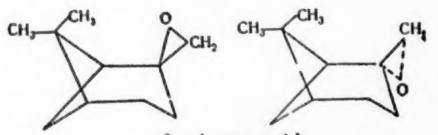
α-pinene β-pinene Δ^3-carene

Comparison of the PMR spectra of the oxides of bicyclic terpenes with the spectra of the original bicyclic hydrocarbons shows that in the case of the oxides the chemical shifts corresponding to the gem-dimethyl groups have high values and retain different values for each of the gem-methyl groups (63.8 and 59.3 for the oxide of α-pinene, 63.2 and 59.6 for the oxide of β-pinene and 65.4 and 62.4 for the oxide of Δ^3-carene). Thus diamagnetic shifts for one of the gem-methyl groups also occur in the case of the oxides. Obviously in this case the diamagnetic shifts are due to the epoxide ring and may give some indication of the conformation of the oxides of bicyclic terpenes.



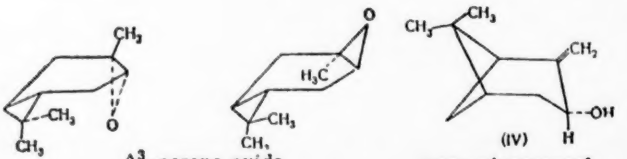
α-pinene oxide

interaction no interaction



β-pinene oxide

interaction no interaction



Δ^3-carene oxide trans-pinocarveol

interaction no interaction

We also studied the PMR spectra of two alcohols of the bicyclic series. The spectrum of trans-pinocarveol is presented in Fig. 4; it has the following chemical shifts: 23.1 (1); 25.5 (1); 29.5 (1); 36.4 (1); 51.7; 60.3 (3) and 66.2 (3). The values 23.1 and 25.5 clearly belong to the methylene groups of the semicyclic bond, the shift at 29.5 to the proton of the hydroxyl group which is indicated by the addition of methyl alcohol to the sample. The shift at 36.4 belongs to the proton at the carbon to which the hydroxyl group is attached. This latter fact emerges from a comparison with literature data for analogous groupings [9]. The protons of the methylene groups and the protons of the picean group contribute to the peak at 51.7. The absorption lines at 60.3 and 66.2 corresponds to the methyl protons of the gem-dimethyl group. One of the methyl groups shows a diamagnetic shift in this case as well (see formula IV). The spectrum of semicyclic carenol consists of blurred lines and the analysis was not therefore completed.

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THE COMPOSITION AND STRUCTURE OF THE COMPOUND OF TITANIUM WITH CHROMIUM

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The A. A. Baikov Institute of Metallurgy, Academy of Sciences of the USSR
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With regard to the special physicochemical properties of titanium and its alloys, these find wide application in many branches of modern technology. Detailed research into the character of the interaction of titanium with various metals and the nature of the phases formed thereby is of importance in the search for new alloys based on titanium [1-4].

The phase diagram for the system Ti–Cr has been studied by a series of authors [5-9]. It has been established that the continuous β solid solutions formed in this system decompose below the solidus line into a series of phases. At the same time at a temperature of about 1350° a chemical compound is formed (Fig. 1). This compound has a face-centered cubic lattice of the $MgCu_2$ type with a parameter equal to a = 6.929 A [4]. There are differences of opinion in the literature regarding the composition of this compound. Some authors give the formula of the compound as $TiCr_2$ [4], and others as Ti_2Cr_3 [9].

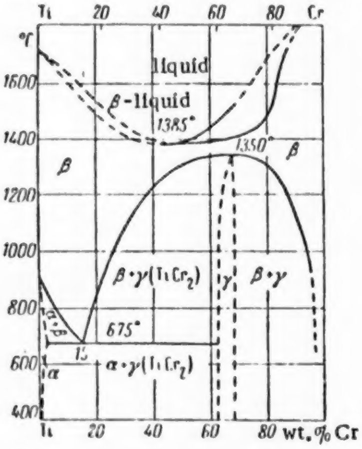

Fig. 1. Phase diagram of the system Ti–Cr.

In the present work the results of a study of titanium/chromium alloys of several compositions containing from 1.0 to 80 weight% of chromium and including the chemical compound as one of the phases are presented. The compositions of the alloys studied are given below. The method used by us previously of anodic solution of the alloys accompanied by the separation of the chemical compound in the form of an insoluble portion followed by an analytical and x-ray study of it was employed.

The alloys were obtained by melting the components together in an arc furnace* and were further subjected to heat treatment. All the alloys were cooled from 600° to room temperature in the furnace. The heat treatment conditions in relation to the phase diagram were as follows:

Alloy composition	Heating time, hours			
weight % Cr	at 1200°	at 1000°	at 800°	at 600°
10-45	4	–	100	600
55	4	–	200	–
70	4	24	100	–
80	4	24	100	–

The alloys prepared in this manner underwent anodic solution under conditions described by us previously [11-16]. For titanium/chromium alloys we first used an electrolyte proposed by N. I. Blok [10], consisting of 2 g KCNS, 10 g citric acid added to 1200 ml of methanol with severe cooling.

The recommended anode current density was 0.013 amp/cm² with the anode placed in a cellulose acetate bag.

The orientation experiments we carried out with the electrolyte mentioned above showed that the anode powder consisting of the alloys which we were investigating did not separate at an anode current density of 0.013 amp/cm². It was established by subsequent experiments that a residue could be separated at a density of 0.03 amp/cm². In this

* The alloys were prepared and supplied to us by T. S. Chernova.

case we obtained anode powders in which, according to chemical and x-ray analysis data, the compound $TiCr_2$ was revealed.

As a result of the investigation we have proposed a new composition for the electrolyte for isolating the compound $TiCr_2$ from titanium/chromium alloys. Composition of the electrolyte: 5 ml HCl (1.19), 3 g succinic acid, 1000 ml methyl alcohol [11]. The electrolyte does not require prior cooling or cooling during the electrolysis process which is the great advantage of the proposed method At the same time bags of lime are used, which are extremely convenient for the process of anodic solution in an acidic electrolyte. The electrolyte enables the metal compound to be separated from alloys with a high chromium content. In order to find the optimum electrolyte composition we carried out measurements of the anode potentials of an alloy close in composition to the pure compound $TiCr_2$ and containing 70 weight % chromium. The measurement was carried out with respect to the saturated calomel electrode [11-13] by the compensation method (Fig. 2). The measurements were made at the instant of applying current and thereafter after definite intervals of time. Prior to each measurement the surface of the alloy electrode was polished and washed with alcohol.

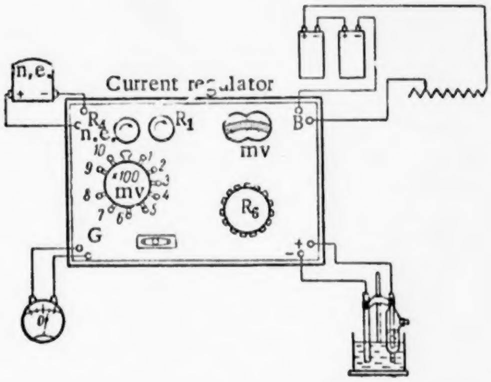

Fig. 2. Arrangement for the measurement of the electrode potential of the sample (anode) by the compensation method.

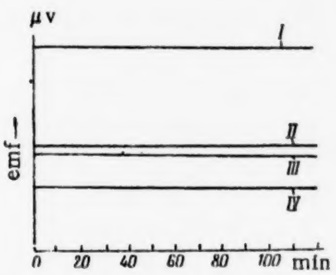

Fig. 3. The electrode potentials of a Ti–Cr alloy (Cr – 70%) in various electrolytes: I) Methanol 1000 ml, 5 ml HCl, 3 g succinic acid; II) electrolyte II; III) electrolyte I; IV) electrolyte III.

As seen from the values obtained (Fig. 3) the anode potential in all the electrolytes tested was established immediately and remained stable, which was confirmed by the anode polarization curve obtained during the anodic solution of the alloy. We carried out experiments to study the solubility of the anode powder containing the pure $TiCr_2$ phase (alloy with 20% Cr) in the proposed electrolyte. Microchemical analysis of the electrolyte was carried out after 30 min, 60 min, 1.5 hr and 24 hr from the commencement of solution of the anode powder at $t = 21°$. Ti and Cr were not found in the solutions investigated. Similar experiments were carried out with an anode of a powdered alloy (Cr 65%), close in composition to the compound $TiCr_2$. The alloy did not dissolve anodically in this electrolyte which testifies to the high selectivity of the electrolyte.

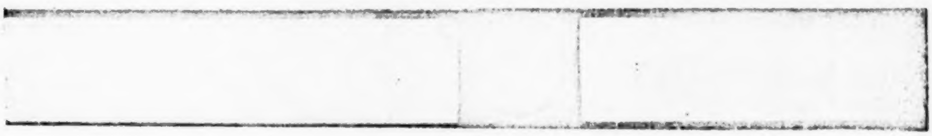

Fig. 4. X-ray radiogram of alloy.

The experiments carried out in other electrolytes also yielded satisfactory and readily reproducible results (Table 1).

In all the experiments the ratio of the chromium to the titanium content corresponded to the theoretical value, equal to 2.0 (atom %) or 2.17 (weight %).

The experiments carried out specially to study the effect of anode current density (Table 2) on the solution of the $TiCr_2$ phase showed that the optimum anode current density lay between the limits of 0.03-0.1 amp/cm^2. In all experiments a compound of stoichiometric composition $TiCr_2$ was formed at the anode as an insoluble component. Electrolyte composition: 5 ml HCl (1.19), 3 g succinic acid, 1000 ml methanol.

TABLE 1. Results of the Microchemical Analysis of the Anode Powders Obtained in Various Electrolytes (duration of experiment 1.5 hr; current density 0.1 amp/cm^2; titanium alloy investigated contained 20% Cr)

Electrolyte	Found in anode powder, weight %		Sum of Cr and Ti, weight %	Cr: Ti weight %	Found in anode powder, atom %		Sum of Cr and Ti, atom %	Cr: Ti atom %	Compound composition
	Cr	Ti			Cr	Ti			
I	68,63	31,37	100,00	2,18	66,83	33,17	100,00	2,01	$TiCr_2$
II	68,37	31,61	99,98	2,16	66,65	33,35	100,00	1,99	$TiCr_2$
III	68,34	31,59	99,93	2,16	66,58	33,42	100,00	1,99	$TiCr_2$

Note: Electrolyte I: 3 ml H_2SO_4 (conc.), 1000 methyl alcohol, 3 g ascorbic acid; electrolyte II: 3 ml H_2SO_4 (conc.), 1000 ml methyl alcohol, 3 g succinic acid; electrolyte III: 5 ml HCl (1.19), 1000 ml methyl alcohol, 3 g salicylic acid.

TABLE 2. Effect of Current Density on Anodic Separation of the $TiCr_2$ Phase (duration of experiment 1.5 hr; the alloy contained 20 weight % Cr)

Current density, amp/cm^2	Weight of powder collected, g	Found, weight %			Found, atom %			
		Cr	Ti	total	Cr	Ti	total	Cr : Ti
0,03	0,0102	68,29	31,55	99,84	66,59	33,40	99,99	1,99
0,05	0,0098	68,64	31,49	100,13	66,75	33,25	100,00	2,00
0,10 *	0,0118	68,27	31,65	99,92	66,51	33,48	99,96	1,99

* The yield of the phase was equal to 16.18 weight %.

Anodic solution of titanium alloys containing chromium (1.0-80%) was carried out. In our experiments the total volume of electrolyte was 1000 ml. The duration of the runs was 1.5 hr. On completion of solution the anodic residue was cleaned off, centrifuged, then washed three times while centrifuging with distilled water and twice with alcohol while decanting. After centrifuging, drying of the centrifuge tube containing the anode residue was carried out in a stream of hydrogen in a large diameter quartz tube placed in an oil bath at 160°. When it reached this temperature heating was stopped but the passage of hydrogen was continued for 3 hr. The dried powder was analyzed by microchemical and x-ray methods. Electrolyte composition: 5 ml HCl (1.19), 3 g succinic acid, 1000 ml methyl alcohol (Table 3).

To carry out the microanalysis of the anode powder for chromium and titanium content a sample of 0.005 g was weighed out on a microbalance, dissolved in H_2SO_4 (1 : 2), acidified with HNO_3 (1.40) and boiled twice until sulfuric acid vapor was evolved. To determine titanium the latter was precipitated with a 6% solution of cupferron after which the analysis was completed colorimetrically with hydrogen peroxide. The determination of chromium was carried out on a separate 0.01 g sample without separating titanium on solution in H_2SO_4 (1 : 6) according to the method described in [14].

As may be seen from the data of Table 3, a metal compound of stoichiometric composition $TiCr_2$ separates from alloys containing from 1.0 to 80% Cr, when these are anodically dissolved.

The x-ray analysis results * (Fig. 4) confirm the existence of a $TiCr_2$ phase (the alloy contained 20% Cr). Chemical materials balance on the electrolysis products with respect to the loss in weight at the anode: current density 0.1 amp/cm^2, electrolyte 5 ml HCl (1.19), 3 g succinic acid, 1000 ml methyl alcohol. Weight of dry anode

* X-ray analysis was carried out at the Central Scientific-Research Institute for Technical Machines.

powder: 0.0406 g. Found in electrolyte after phase separation: Ti 0.1750 g, Cr 0.0167 g, total 0.2323. Loss in weight at anode 0.2399 g.

TABLE 3. Results of Microanalysis of the Anode Powders (duration of experiment 1.5 hr; current density 0.1 amp/cm^2)

Cr content in alloy as charged, weight, %	Cr content in alloy by chem. analysis, weight, %	Found in anode powder weight %		Sum of Cr and Ti, wt., %	Cr : Ti ratio, weight %	Found in anode powder atom %		Sum of Cr and Ti, atom %	Cr : Ti ratio, atom %	Results of x-ray analysis***
		Cr	Ti			Cr	Ti			
1,0	0,95	68,35	31,81	100.17	2.15	66,15	33,85	100,00	1,95	$TiCr_2$
2,0	2,12	68,57	31,22	99,99	2,19	66,96	33,05	100,01	2,01	$TiCr_2$
10,00 *	10,12	68,53	31,38	99,91	2,17	66,86	33,14	100,00	2.010	$TiCr_2$
15,50	15,65	68,45	31,60	100,05	2,16	66,61	33,39	100,00	1,994	$TiCr_2$
17,50	17,37	68,42	31,55	99,97	2,16	66,63	33,36	99,99	1,997	$TiCr_2$
20,00 **	19,89	68,61	31,43	100,04	2,18	66,78	33,21	99,99	2,010	$TiCr_2$, $TiCr_2$
30,0	30,22	68,45	31,48	99,93	2,17	66,70	33,30	100,00	2,000	$TiCr_2$
45,0	45,05	68,38	31,56	99,94	2,16	66,62	33,37	99,99	2,000	$TiCr_2$
65,0	64,80	68,80	31,33	100,13	2,19	66,59	33,41	100,00	1,99	$TiCr_2$
70,0	69,52	68,34	31,52	99,86	2,16	66,60	33,40	100,00	1,96	$TiCr_2$
80,00	79,68	68,45	31,64	100,09	2,16	66,48	33,41	99,89	1,990	$TiCr_2$

* Yield of this phase 16.72%.

** Yield of this phase 16.88%.

*** X-ray analysis carried out at the Central Scientific-Research Institute for Technical Machines.

The investigation carried out on titanium/chromium alloys of a range of chromium contents from 1.0 to 80% showed the existence of a metal compound $TiCr_2$ in the alloys.

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THE OCCURRENCE OF EXCHANGE BETWEEN IRRADIATED METALLIC PLATINUM AND COMPLEX IONS OF BIVALENT PLATINIUM IN AQUEOUS SOLUTIONS

Academician A. A. Grinberg, M. I. Gel'fman, E. N. In'kova, and G. A. Shagisultanova

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As has been shown by two of us [1], when the potential of a platinum electrode is measured in solutions of complexes of bivalent platinum, the platinum electrode behaves not as an inert electrode but as one which affects the concentration of Pt^{2+} ions. The detailed mechanism of the corresponding reaction was not established but the suggestion was put forward that an exchange of platinum between the electrode and the complex ions takes place [2].

In order to check this suggestion the experiments described below were carried out. The irradiated platinum containing the isotope Pt^{197} was in the form of two pieces of sheet each about 0.3 g in weight; the total radioactivity of each sample was about 2.5 millicuries. The pieces of irradiated metal after washing with water were placed into 50 ml 1 M KCl solution (a) and 50 ml of a 1 M KCl solution containing 0.45 g chloroplatinate $K_2[PtCl_4]$ (b), respectively. The solutions containing the platinum were agitated for 2 hr. On completion of the agitation 20 ml samples of the solutions were taken and measured in special vessels with an AS-1 type β counter.

In the case of the KCl solution 190 counts/min had been transferred to the solution, while in the case of the solution containing $K_2[PtCl_4]$ 565 counts/min above the background level. These solutions were used to evaluate the half-life of the metal which had passed into solution. For solution (a) the value was approximately 25 hr,* while for solution (b) it was approximately 20 hr. The half-life for Pt^{197} according to published data is 18 hr. Agitation of the platinum strip in the same solutions was then continued. Agitation in solution (a) was continued for another 3 hr, and in solution (b) for 2 hr. 290 counts/min were detected in the KCl solution, and 726 counts/min in the solution containing chloroplatinate. All figures are referred to the time of commencement of the experiment.

The solution with $K_2[PtCl_4]$ was precipitated (after the second agitation) by an excess of the chloride of Reise's Base $[Pt(NH_3)_4]Cl_2$. The precipitated green Magnus salt was filtered, washed with alcohol and ether and dissolved in KOH solution with heating. The radioactivity of the Magnus salt solution and also of the filtrate obtained from the salt and the wash liquors was measured as indicated above. The following data were obtained from this measurement: 545 counts/min in the Magnus salt solution, 262 counts/min in the filtrate. The sum of the measured radioactivities agrees satisfactorily within the limits of experimental error with the radioactivity of the original solution.

A half-life determination was carried out for the process of dissolving the Magnus salt in alkali and the half-life was found practically to coincide with the published data (18 hr).

This experiment showed that approximately two-thirds of the total platinum passing into solution was in a form which could be precipitated by the $[Pt(NH_3)_4]^{2+}$ ion. The fact that a portion of the platinum was not precipitated in the form of Magnus salt may be explained by the fact that in the reaction of the platinum strip with the solution we used, not only $[PtCl_4]^{2-}$ ions are formed but also some other types which are not precipitated by the tetrammine, for example $[Pt(Cl_2(H_2O)_2]$.

By means of special experiments with $K_2[PtCl_4]$ with labelled platinum it was shown that in the formation and decomposition of the green Magnus salt no exchange of the central atoms occurs. The Magnus salt was precipitated from a solution containing 0.14 g $K_2[PtCl_4]$ with radioactive platinum (Pt^{197}). 0.2 g of the Magnus salt was carefully ground

* The somewhat increased value of the half-life of platinum obtained in the KCl solution can be explained by the presence of traces of the radioactive isotope of gold Au^{199} which is present as an impurity.

in a mortar, after which it was left in the dark for a long time. After 18 hr the Magnus salt was decomposed with a solution of 0.113 g $AgNO_3$. The precipitate of $Ag_2[Pt^{197}Cl_4]$ was filtered off and carefully washed with water. Measurements showed that the entire initial quantity of radioactive platinum was concentrated in the $[PtCl_4]_2$-ion, i.e., exchange of the central atoms between $[Pt(NH_3)_4]^{2+}$ and $[PtCl_4]^{2-}$ did not occur.

On completion of the second agitation of the platinum strip with the KCl solution the platinum strip was carefully washed with distilled water and placed in 50 ml of 0.05 M ammonia solution containing 0.2 g of tetrammino-platinochloride $[Pt(NH_3)_4]Cl_2$ and 3.8 g $NaNO_3$ (solution c). Agitation was continued for 2 hr. 153 counts/min passed into solution. After a second period of agitation for 3.5 hr the radioactivity reached 336 counts/min. The solution was then separated from the platinum and precipitated with an excess of $K_2[PtCl_4]$. The Magnus salt obtained, as in the previous case, was dissolved in hot KOH. The radioactivity of the alkaline solution of the Magnus salt was found to be equal to 159 counts/min, and the radioactivity of the filtrate 121 counts/min. Considering the small values of the radioactivity, the balance must also be considered satisfactory in this case. It follows from this experiment that about one half of the platinum passing into solution was present in the form of $[Pt(NH_3)_4]^{2+}$ ions. It was established by the same experiment that ions of the stated composition are in fact formed from metallic platinum. An order-of-magnitude estimate indicated that the amount of platinum which passed into solution in our experiments was of the order of 10^{-8} g. The fact that the process of the formation of $[PtCl_4]^{2-}$ and $[Pt(NH_3)_4]^{2+}$ ions in the conditions described did not go to completion appears to be quite natural since not only Cl^- ions and NH_3 molecules but also solvent molecules may attach themselves to the Pt^{2+} ion at the surface of the strip. It is possible that if hydrochloric acid had been used instead of KCl or if the ammonia concentration had been higher the extent of the formation of $[PtCl_4]^{2-}$ and $[Pt(NH_3)_4]^{2+}$ ions respectively would have been greater. The solutions which we employed in these experiments corresponded to the solutions encountered when the potentials of the platinum electrodes were measured [1, 2].

The results of our experiments in conjunction with the data of the references quoted are evidence to the effect that an exchange between the platinum strip and the $[PtCl_4]^{2-}$ and $[Pt(NH_3)_4]^{2+}$ ions did in fact take place under the conditions described. As regards the mechanism of this exchange, one possible route for it is a process of the type which we put forward in a previous study [2]. In the case of platinite systems it is also possible to envisage that the exchange occurs due to reaction with the metallic platinum of the platinite which forms in the solution during the process of the disproportionation of a platinite. We are aware that in the process of irradiating metallic platinum a change in the nature of the surface layer, in particular, the formation of surface oxides could occur. However the potential measurements in the solutions mentioned were also carried out with a platinized electrode, i.e., under conditions in which an active surface was present.

Subsequently we propose to carry out experiments to elucidate the occurrence of exchange with irradiated platinum previously subjected to reduction.

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METALLIC COMPOUNDS IN THE REGION OF THE α SOLID SOLUTIONS OF THE TITANIUM-ALUMINUM SYSTEM

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The A. A. Baikov Institute of Metallurgy, Academy of Sciences of the USSR
(Presented by Academician I. I. Chernaev, October 27, 1960)
Translated from Doklady Akademii Nauk SSSR, Vol. 137, No. 3, pp. 599-602, March, 1961
Original article submitted October 7, 1960

As a result of the researches of numerous authors [1-5] the phase diagram for the binary system titanium-aluminum is shown to be characterized by an extensive region of solid solutions based on the α and β modifications of titanium. According to the data of microstructure and x-ray studies the region of the α solid solution of aluminum in titanium extends from 0 to 25 weight % aluminum and the temperature of the polymorphic phase change $\alpha \rightarrow \beta$ increases with aluminum content. Alloys in the region of the α solid solutions are characterized by a densely packed hexagonal lattice.

Simultaneously with the study of the phase diagram of titanium-aluminum alloys we carried out the determination of their properties. In the investigation of the flow of alloys by deformation to the yield point by the centrifugal force method [6] it was established that their resistance to flow increased sharply accompanied by simultaneous fall in plasticity within the limits of 7.5 to 20 weight % aluminum content.

These changes in the properties of alloys of the binary system titanium-aluminum in the solid solution region could not be explained by the normal methods of metallographic analysis.

The aim of the present study was the investigation of the α solid solution region in the titanium-aluminum system and the confirmation of the nature of the phases present by the technique of measuring the Hall coefficient [7, 8] as a function of the composition of the alloys.

Data obtained previously [9, 10] has shown that electromagnetic effects are linked with the composition of various alloys in such a way that break points and discontinuities are revealed on a plot of composition against Hall coefficient. Break points correspond to the stoichiometric compositions of chemical compounds. This phenomenon is explained by the fact that on application of a magnetic field there occurs a change in the states of the external electron envelopes of the atoms, which affects the behavior of the conductivity electrons producing a change in the Hall constant.

Galvanomagnetic effects are directly connected with the behavior of the electronic components of the peripheral envelopes of atoms, and therefore it is possible with their aid to study in an extremely sensitive manner the state of the periphery of the atoms and thus to elucidate the nature of the chemical bond between the different atoms of metallic alloys.

EXPERIMENTAL

A series of alloys with different contents of the components was prepared from pure metallic titanium and aluminum (from 0 to 40 weight % aluminum). The alloys were prepared by two methods: 1) The powder metallurgy method, by pressing specially shaped samples followed by sintering under vacuum in accordance with the following schedule: 1000°–100 hr, 800° – 50 hr, 600° – 100 hr; 2) the technique of melting in an arc furnace with a nonexpendable tungsten electrode followed by the preparation of samples for Hall constant determination in the form of 10 x 30 x 1.5 mm disks and of electrical contacts of triangular shape. The electrical contacts were knife-edged at the point of contact with the sample and could be slid across the polished surfaces of the samples with the aid of micrometer screws.

The testing technique and the arrangement of the apparatus have been described in the literature [11]. The mean values obtained for the Hall constant measurements on sintered cast and annealed alloys are presented in the table.

Data on the Hall Constants of Sintered, Cast, and Annealed Alloys of the Titanium-Aluminum System

Al content, %	Hall constant × 10^{-12} of alloys		
	sintered	cast	cast and annealed
0	0	0	0
4,36 a 2,5 w	0,062035 ± 0,026	0	
8,52 a 5,0 w	0,223999 ± 0,015	0	
10,16 a 6,0 w	0,268054 ± 0,6141	0,15434 ± 0,0150	0,193491 ± 0,0141
12,60 a 7,5 w	—	0,1170503 ± 0,045	0,293334 ± 0,0178
13,45 a 8,0 w	—	0,2474267 ± 0,185	0,1865846 ± 0,0106
14,14 a 9,0 w	—	0,6823133 ± 0,0120	0,51303 ± 0,120
16,51 a 10,0 w	0,562180	0,731783 ± 0,0215	0,7808003 ± 0.170
17,25 a 11,0 w	—	0,5795207 ± 0,0492	1,228103 ± 0,0714
19,57 a 12,0 w	—	—	0,92553
20,0 a 12,5 w	4,45879 ± 0,173	—	
20,91 a 13,0 w	—	2,10010 ± 0,0180	2,080289 ± 0,161
22,41 a 14,0 w	3,43710 ± 0,170	2,33797 ± 0,157	2,17404 ±0,0512
23,95 a 15,0 w	4,115600 ± 0,187	4,40590 ±0,1345	4,387189 ± 0,200
25,10 a 16,0 w	3,887287 ± 0,228	2,70210 ± 0,172 2,79959 ± 0,132 2,554097	2,756826 ±0,080
26,62 a 17,0 w	—		
28,07 a 17,5 w	2,8075 ± 0,0871		2,86689 ± 0,178
30,83 a 20,0 w	2,63763 ± 0,0162	2,755197 ± 0,0244	
33,39 a 22,0 w	2,4460 ± 0,0266	—	2,218308 ± 0,0836
34,05 a 22,5 w	2,102906 ± 0,0[illegible]3	2,1344980 ± 0,310	2,161103 ± 0,0153
34,68 a 23,0 w	2,391420 ± 0,220		
35,95 a 24,0 w	2,27879 ± 0,0719		
38,72 a 26,0 w	2,71220 ± 0,208		
39,68 a 27,5 w	1,506357 ± 0,0261		
21,11 a 30,0 w	0,745089 ± 0,0264		
46,16 a 33,0 w	—	0,3479517 ± 0,103	
50,00 a 36,0 w	—	0,3035150 ± 0,151	
51,53 a 38,0 w	—	1,172150 ± 0,0518	
53,85 a 40,0 w	—	1,183276 ± 0,167	

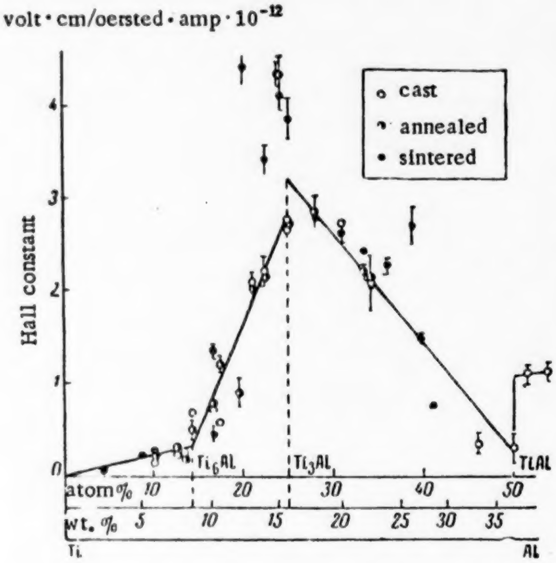
Note: a) atom percent, w) weight percent.

A graph is constructed in the figure from the data of the table showing the dependence of Hall constant on composition for alloys prepared from powdered titanium; two jumps from one linear variation of Hall constant to another can be observed in the figure. The first of these breaks corresponds to the compound Ti_6Al, 14.3 atom % (9 weight %) aluminum,. and the second to the compound Ti_3Al, 25 atom % (16 weight %) aluminum. The results of the Hall constant measurements for cast alloys, presented in the table and figure, do not differ in principle from the results of the investigation of the sintered alloys (figure).

The compounds Ti_6Al and Ti_3Al revealed in the sintered alloys are confirmed by the study of the variation of Hall constant with composition for the cast alloys. The cast alloys were subjected (after measurement of the Hall

effect) to a homogenizing heat treatment to attain equilibrium at 900° – 200 hr, 800° – 300 hr, 600° – 350 hr.

The results of the Hall constant measurements on the annealed alloys are given in the table and the figure. The variations of Hall constant with composition for annealed alloys of the titanium-aluminum system were of a similar nature to those of the sintered and cast alloys. Jumps at the break points are observed at the same stoichiometric compositions of the compounds as for both sintered and cast alloys.



The limited region of α solid solutions, in which two metal compounds occur, presents considerable difficulties in determining the precise pattern of the variation of the Hall constant, as this determination demands a very high precision of measurement. The required precision was achieved with the present apparatus.

Three series of alloys prepared by different methods were studied in order to check these results. The over-all results agree completely with one another in spite of some divergences in the magnitude of the Hall effect for alloys similar in composition but prepared by different methods.

Solid solutions of aluminum in α-titanium are distinguished by a complex type of interaction, the basic reason for which is the occurrence of the two compounds, Ti_6Al and Ti_3Al. These compounds appear to have a hexagonal lattice, are formed from the solid solutions and correspond to compounds of the Kurnakov type [12].

We also determined the values of the Hall constant for alloys of the titanium-aluminum system in the γ phase region. Alloys were investigated in the γ phase region having compositions corresponding to: 46.16 atom % (33 wt %), 50.0 atom % (36.02 wt %), 51.53 atom % (38.0 wt %) and 53.85 atom % (40.0 wt %) aluminum.

A sharp break in the Hall effect–composition curve was observed at the composition of the alloy with 50.0 atom % (36.02 wt %) aluminum, corresponding to the compound TiAl, confirmed by alternative physicochemical analysis methods.

The equilibrium state of these compounds and the regions over which they extend on the phase diagram of the titanium-aluminum system depend on the conditions and the kinetics of their formation. These problems require additional study. The occurrence of the compounds Ti_6Al, Ti_3Al and TiAl in this system accounts for the increased heat resistance and the sharp drop in the plastic properties of titanium alloys containing more than 7-8 wt % aluminum.

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THE CONNECTION BETWEEN UNSATURATION AND RATE OF AUTO-OXIDATION IN MIXTURES OF TRIGLYCERIDES OF NATURAL FATS

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The N. I. Pirogov Second Medical Institute
(Presented by Academician B. A. Kazanskii, November 12, 1960)
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Original article submitted November 10, 1960

It is a common opinion that the greater the unsaturation of a mixture of fat triglycerides, expressed by the value of the iodine number, the higher the rate of auto-oxidation of natural fats, if the effect of oxidation inhibitors and promotors is discounted [1]. Such an appraisal of the readiness of fats to undergo oxidation is primarily based on a comparison between the ability of vegetable fats with a high iodine number (drying oils) to oxidize rapidly and the comparative inertness to oxidation of solid animal fats with low iodine numbers.

As the relationship between auto-oxidation rate and the degree of unsaturation of naturally occurring triglyceride mixtures has not been studied in detail for fats of the same type, the connection between oxidation rate and iodine number for different samples of a naturally occurring fat having a triglyceride composition of the same type was investigated in the present work. Mixtures of triglycerides of pork fat were chosen as the subject of research, in view of the fact that the content of unsaponifiables is very low in this fat (about 0.3%) and the triglycerides of this fat are, practically speaking, not protected from oxidation by the presence of inhibitors.

The samples of pork fat were separated from the tissue at 60° in an atmosphere of nitrogen and determination of iodine number IN, by the method of Rosenmund and Kuhnhenn [2], and of thiocyanogen number TN were carried out on them; the mean molecular weight of the triglycerides referred to one double bond was calculated by the formula

$$M_m/\Delta = \frac{I_2 \times 100}{IN}$$

where M_m is the mean molecular weight, and Δ is the number of double bonds and the triglyceride composition was evaluated applying the well-known Kaufmann equations by a method developed by us on a previous occasion [3]. The results of the stated determinations are given in the table.

Sample No.	Iodine number	Thiocyanogen number	M_m/Δ	Triglyceride fractions, %		
				saturated acids	oleic acid	linoleic acid
1	30,10	29,90	842,5	65,38	34,36	0,26
2	32,40	31,80	783,0	63,16	36,15	0,69
3	34,52	33,20	735,3	60,50	38,18	1,55
4	42,90	38,40	591,6	55,50	39,40	5,20
5	46,20	44,10	549,4	48,50	49,30	2,20
6	53,40	49,00	475,3	43,26	50,82	6,23
7	56,20	34,80	451,6	60,32	15,47	24,54
8	64,00	45,30	396,6	47,54	31,00	21,60
9	70,40	58,30	360,5	32,48	53,74	13,68

The fat samples obtained with different iodine numbers were poured rapidly and simultaneously into completely identical Petrie dishes to form layers of equal thickness and were left to stand in air at 20° in diffused sunlight. Every 12 hr samples were taken to check for the appearance of low-molecular-weight acids in the auto-

oxidation products using the neutral red reaction in accordance with the Schonberg method [4]. This reaction was checked by a highly sensitive test for the appearance of physiologically detectable signs of severe oxidation. As a rule, the results of the stated tests of the extent of changes brought about by oxidation give good agreement.

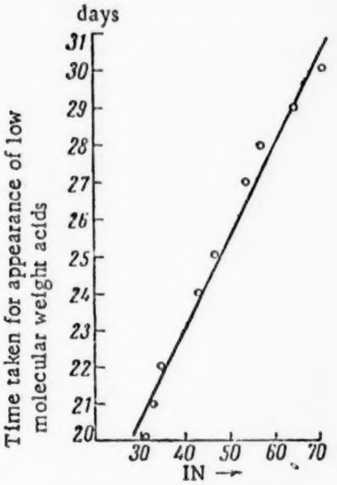

Fig. 1. Auto-oxidation rate of a mixture of pork fat triglycerides.

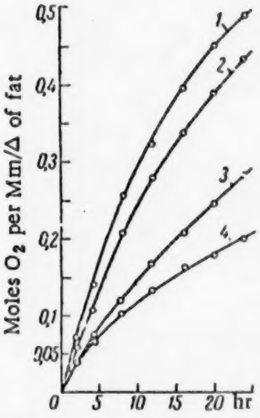

Fig. 2. Intensity of oxygen absorption by samples of pork fat with different iodine numbers: 1) 30.1; 2) 32.4; 3) 55.4; 5) 65.8.

The results of the auto-oxidation experiments carried out are illustrated in Fig. 1, from which it can be seen that contrary to the usual ideas the rate at which the indications of the changes brought about by severe oxidation appear, i.e., the rate of auto-oxidation of a mixture of pork fat triglycerides, decreases with increase in iodine number. Indeed on comparing the results obtained with the data of the table it can be seen in addition that the intensity of oxidation of a mixture of pork fat triglycerides is directly proportional to the mean molecular weight of the triglycerides based on one double bond, i.e., M_m/Δ.

In order to confirm this conclusion, experiments were carried out to determine the intensity of oxygen absorption by pork fat samples with different iodine numbers. A method described by us previously [5] which enables auto-oxidation to be carried out at a constant oxygen concentration in the gas phase was employed for these experiments. The experiments were carried out at 60° in weak diffused sunlight for a period of 24 hr. The results of experiments with fat samples having the following iodine numbers: 30.10; 32.40; 55.40 and 65.80, expressed in moles of oxygen absorbed per M_m/Δ of fat are illustrated in Fig. 2 in the form of curves.

From a comparison of the curves in Fig. 2 it can readily be seen that molar oxygen absorption based on one double bond (and consequently the intensity of auto-oxidation) decreases with increase in iodine number. From this it follows that the extent of the changes brought about by oxidation does not depend on the number of double bonds per unit weight, i.e., not on the iodine number IN, but on the distribution of the double bonds within the molecules of the fat triglycerides.

The results obtained show that this distribution of unsaturated bonds, at least in the case of pork fat, apparently corresponds to the principle of the uniform distribution of residues of unsaturated acids, particularly oleic acid, in the triglycerides of which the fat is composed. This principle merits attention alongside the principles of the ordered (equal) and probable (random) distributions of fatty acid residues in the triglycerides of naturally occurring fats which are already well-known [6] and under discussion.

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THE ORDER OF THE ADDITION OF LITHIUM TO DIPHENYL

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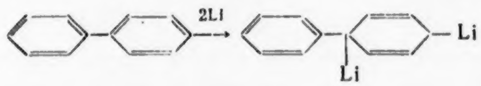
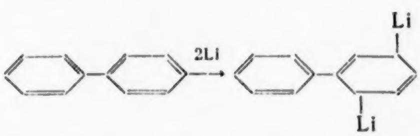
Original article submitted December 21, 1960

It has been shown by A. D. Petrov and T. I. Chernysheva [1] that when trimethylchlorosilane and tributylchlorosilane are reacted with dilithiumdihydrodiphenyl, in the first case monotrimethyldisilyldihydrodiphenyl and in the second ditributylsilyldihydrodiphenyl are formed.

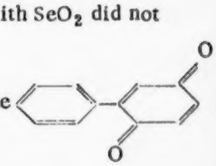
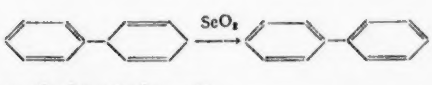
On condensation of dilithiumdihydrodiphenyl with alkyl halides [2] (n-butyl-, n-hexyl-, sec-octyl-, 2-ethylhexyl, n-nonyl-, and n-decylbromides) we obtained both the monoalkyldihydrodiphenyls and the dialkyldihydrodiphenyls. However the problem of the point at which the lithium attaches itself to diphenyl and consequently of the most probable location of the alkyl substituents in dialkyldihydrodiphenyls has remained unclarified. According to Schlenk and Bergman [3] attachment of the lithium to diphenyl occurs in the 1:4 position



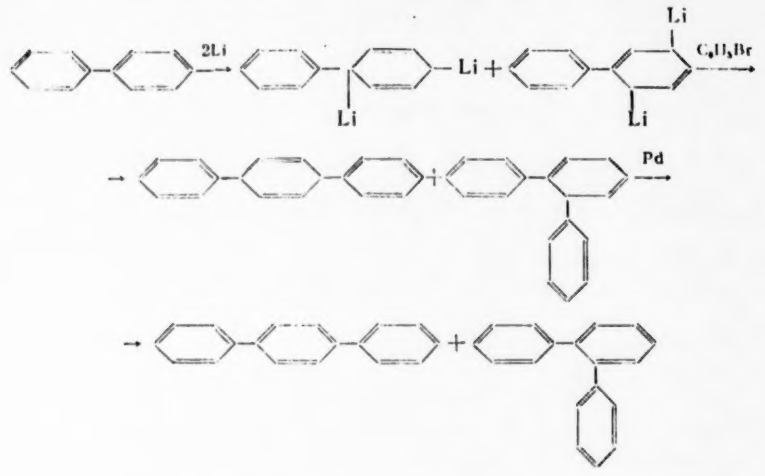
According to spectroscopic analysis [4] in the case of the mono- and dialkyldihydrodiphenyls and hydrodiphenyls obtained by us the addition of lithium to diphenyl predominantly occurs in the 2,5 position



In the present study we have attempted to confirm the point of attachment of the lithium to diphenyl in two ways: by oxidation of dihydrodiphenyl with SeO_2 and by condensation of dilithiumdihydrodiphenyl with bromobenzene yielding easily identified terphenyls. If the addition of lithium occurs at the 1,4 position, we should obtain as a result of the addition of a phenyl group p-terphenyl having a m. p. of 210°. If the addition of lithium occurs at the 2,5 position, we should obtain o- or m-terphenyls of melting point 56 and 84°, respectively.

The first method of confirmation proved to be unsuccessful: oxidation of dihydrodiphenyl with SeO_2 did not yield the products expected or phenylcyclohexadienone , or phenylquinone , but dihydrodiphenyl was reduced to diphenyl  in a similar manner to the oxidation of 9,10-dihydroanthracene as described by Bedger [5].

On reaction of bromobenzene with dilithiumdihydrodiphenyl followed by dehydrogenation of the product over carbon-supported Pd a mixture of terphenyls was obtained at a yield of 6-15%. We separated o- and p-terphenyl by a technique for separating the still residues obtained in the pyrolysis of benzene, which we developed earlier [6].



We were unable to isolate m-terphenyl. We evidently encounter here a situation analogous to the bromination of toluene where, as is well-known, only the o- and p-isomers [7] are formed. Depending on the temperature of the experiment either one or the other isomer predominated; at a reaction temperature of 30°, 50% o-terphenyl was formed, at 0° the p-isomer predominated.

The infrared spectra of the terphenyls produced were obtained on a UR-10 machine using a KBr prism in the 400-700 cm^{-1} range and a NaCl prism in the 700-1400 cm^{-1} range.*

The following bands were detected for o-terphenyl: 500 w, 525 w, 560 m, 615 m, 708 m, 745-455 w, 785 m, 810 w, 845 m, 880 w, 900 m, 920 m, 955 w, 980 w, 1015 m, 1080 m, 1110 w, 1160 w, 1185 w. For p-terphenyl the following bands were obtained: 460, 618, 690, 750, 840, 910, 1010, 1030, 1050, 1080, 1130, 1180.

It may thus be considered that the addition of lithium to diphenyl occurs both at the 1,4 position and at the 2,5 position (the latter compound may be formed by the isomerization of the former).*

EXPERIMENTAL

Oxidation of dihydrodiphenyl with SeO_2. Preparation of dihydrodiphenyl. 77 g diphenyl, 400 ml absolute ether, and 7 g finely divided lithium and some glass beads were placed in a flask filled with nitrogen. The flask was closed with a bung and agitated on a shaker for 100 hr. The reaction flask was then placed in an ice water bath and first alcohol then water were added through a dropping funnel, the ethereal solution was separated, washed with water and dried. After removal of the solvent and freezing out the unreacted diphenyl, the liquid dihydrodiphenyl (15 g) was distilled. It had a b. p. of 84-85° at 4 mm; freezing point 5°; $n^{20}D$ 1.5603; d^{20}_4 0.9925; MR found 50.91, MR calculated for $C_{12}H_{10}$ 51.08.

Three g dihydrodiphenyl, 2 g SeO_2 and 6 ml nitrobenzene were taken. The mixture was heated in a flask with a reflux condenser. Turbidity set in at 50°, vigorous reaction commenced at 80° and the temperature rapidly rose to 125°. The reaction mixture was then heated at 150° for 2 hr. The product was extracted with ether and the Se filtered out. After removing the solvent the product was steam-distilled, and the crystals which separated, after recrystallization from C_2H_5OH, had a m. p. of 68°.

Found %: C 92.81, 92.64; H 6.45, 6.40. $C_{12}H_{10}$. Calculated %: C 93.51; H 6.42.

Reaction of dilithiumdihydrodiphenyl with bromobenzene. 77 g diphenyl, 500 ml absolute ether, 8 g finely divided lithium were placed in a flask filled with nitrogen. Agitation on a shaker was continued for 100 hr. 157 g bromobenzene was then added at 0°. After the usual treatment and removal of the ether, the product was distilled in a column. Obtained (in grams): benzene 25; bromobenzene 55, diphenyl 57; terphenyls 12.5 (11%). In experiments in which the bromobenzene was added to the dilithiumdihydrodiphenyl at −15° and −30°, the terphenyl yield was 5-8 g (5-8%). At 35° the terphenyl yield was 13 g (12%).

* The infrared spectra were determined by E. D. Lubuzh to whom the authors express their gratitude.

Dehydrogenation of terphenyls. Ten g terphenyl and 2.1 g Pd on carbon (20% Pd content) were placed in a long-necked flask fitted with a stirrer and thermometer. The flask was placed in a bath of Wood's metal and heated to 300-335°. Heating was continued for 40 min. After cooling the crystalline produced was extracted with 50 ml benzene at 50°.

Separation of terphenyls. To carry out the separation of the terphenyls the product of several similar experiments were bulked together. The whole mixture was dissolved in benzene at 60°. On cooling the benzene, crystals were precipitated which were recrystallized twice from benzene; these had a m. p. of 203-205°. The mother liquor after separation of the p-terphenyl and the benzene extract after recrystallization were bulked together. The benzene was stripped off, and the oily mass remaining crystallized after a day. These crystals were recrystallized from alcohol; these had a m. p. of 70-72° and according to spectroscopic analysis data consisted of diphenyl with occasional slight contamination with p-terphenyl. Alcohol was stripped from the alcoholic mother liquor after removal of diphenyl and a clear, yellow, mobile liquid, c. p. +5°, remained behind in the flask. This liquid crystallized after standing in a refrigerator for 3-5 days. The crystals, recrystallized from alcohol, had m. p. of 52° and consisted of o-terphenyl.

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THE EFFECT OF OXYGEN AND WATER ON THE HYDROGENATION AND ISOMERIZATION ACTIVITY OF TUNGSTEN SULFIDE CATALYST

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The hydrogen used in various hydrogenation processes normally contains impurities, particularly oxygen. For instance, according to data given by Makarov [1] the circulating gas in industrial plants for liquid phase hydrogenation of heavy oils contains 80-83% H_2, 0.1-0.2% O_2, 0.2-0.4% CO, 0.2-0.3% CO_2, 9-11% hydrocarbons C_nH_{2n+2}, and 7-8% N_2. Industrial electrolytic hydrogen may contain up to 0.5% oxygen.*

The purpose of the present study is to elucidate the effect of traces of oxygen and water on the activity of industrial WS_2 catalyst. To this end an investigation of the hydrogenation of benzene and the isomerization of cyclohexane under hydrogen pressure was carried out in a continuous unit [2]. The technical electrolytic hydrogen we employed contained up to 0.1% oxygen. Hydrogen, compressed to the required pressure, was passed at 300-320° through a tube with granulated copper (250 g; the copper was prepared by prior reduction of copper oxide) to free it from oxygen. The water formed from the oxygen was retained in a drier packed with caustic potash (280 g) and silica gel (110 g). Experiments were carried out both with unpurified hydrogen and with hydrogen freed of oxygen and water. The whole investigation was carried out with one sample of catalyst (28 g, 12 ml) of particle size 3-5 mm. The catalyst was mixed with pieces of porcelain (60 ml) of the same size. The temperature was measured with a chromel/alumel thermocouple, immersed to 25 mm measured from the surface of the catalyst bed (bed depth 190 mm). Before the run the catalyst was kept in a slow stream of hydrogen (approx 2 l/min) for 4 hr at 400° and 250 atm. In this stage the method of hydrogen purification was the same as in the run. The investigation of benzene hydrogenation was carried out at 310°,** 250 atm and at feed rates of 0.60 moles/hour benzene and 15 moles/hour hydrogen. The benzene hydrogenation products were analyzed by the methods of relative dispersion [3] and (in some cases) gas-liquid chromatography. The isomerization of cyclohexane was investigated at 370°, 150 atm and feed rates of 0.11 mole/hour cyclohexane and 2.0 moles/hour hydrogen. Determination of the degree of conversion of cyclohexane to methylcyclopentane and hexanes was carried out by fractionation of the products [2] and occasionally by gas-liquid chromatography. Both methods yielded similar results (the difference in the degree of isomerization determined did not normally exceed 2%). Runs on the hydrogenation of benzene were alternated with runs on the isomerization of cyclohexane. The data obtained are presented in Tables 1 and 2.

The experiments carried out showed that the presence of oxygen and water in the hydrogen caused an extremely substantial drop in the hydrogenation activity of the catalyst and an increase (although not so marked) in its isomerization activity. As may be seen from the data of Tables 1 and 2, runs with hydrogen freed of oxygen and water (Nos. 1-2, 8-12, and 20-24) were carried out on the same catalyst sample alternating with runs using unpurified hydrogen. In all three series of runs with purified hydrogen activation of the catalyst occurred in the hydrogenation of benzene (the degree of hydrogenation increased to 87-93%); in the series of runs with unpurified hydrogen the conversion dropped to 8-13%. Thus the effect observed is reversible. The same applies to cyclohexane isomerization: The extent of this reaction decreased from 34 to 14% as a result of purifying the hydrogen; after taking the purification system off-stream the degree of isomerization again reached its former value.

On changing from runs with purified hydrogen to runs without gas purification (and vice versa) the hydrogenation activity of the catalyst either rapidly stabilized itself (after a sharp change) or changed gradually (see runs Nos. 20-24). The gradualness of the activity change in the stated series of runs was evidently caused by the relatively

* In the runs with a high benzene conversion hot spots were observed in the catalyst bed (see Table 1).
** State Standard No. 3022-45.

long duration of the previous series carried out without gas purification (runs Nos. 13-19) and consequently by the larger quantity of oxygen introduced into the catalyst.

TABLE 1. Hydrogenation of Benzene at 250 atm

Run No.	Hydrogen used	Run temp. °C	Degree of hydrogenation of benzene, %
1	with purification	310-318	84.8
2	" "	301-309	87.5
3	without purification	310-314	56.9
4	" "	308-310	19.6
7	" "	310	13.3
8	with purification	310-134	87.1
11	" "	305-310	92.8
13	without purification	310	15.2
15	" "	310	9.5
16	" "	310	13.9
18	" "	310	8.0
19	" "	310	9.0
20	with purification	309	43.3
21	" "	308-309	65.2
22	" "	310-311	69.7
23	" "	310	83.2
24	" "	309-312	86.6

TABLE 2. Isomerization of Cyclohexane at 370° and 150 atm

Run No.	Hydrogen used	Degree of isomerization of cyclohexane, %
5	without purification	31.0
6	" "	33.8
9	with purification	14.1
10	" "	14.1
12	without purification	34.0
14	" "	32.9
17	" "	34.2

The marked change in the hydrogenation and isomerization activity of the catalyst which we observed with gas purification may be due both to oxygen adsorbed or dissolved in the catalyst (for example in the form of atomic oxygen) and to water formed from the oxygen and adsorbed on the surface. To elucidate this problem we carried out a series of additional benzene hydrogenation and cyclohexane isomerization runs in which the hydrogen drier was left out, and the wet gas from the furnace with the copper entered the reactor through a steel capillary tube, the temperature of which was maintained at 300-320°. In this way the hydrogen was freed of oxygen but the water formed went forward onto the catalyst. The degree of hydrogenation in these runs rose somewhat in comparison with the runs carried out without freeing the hydrogen from oxygen and amounted to 15-22%. The results obtained permit the statement that the hydrogenation activity of the catalyst is depressed not only by the water formed but by oxygen itself. At the same time when the hydrogen purification system was run without the drier no change was observed in the degree of isomerization of cyclohexane in comparison with the runs carried out without any gas purification at all.

Let us attempt first of all to analyze the results obtained in the experiments on benzene hydrogenation. The sharp drop in hydrogenation activity of the WS_2 catalyst on changing to unpurified electrolytic hydrogen was caused to a considerable extent, as we have already seen, by the water formed. It is possible that water, in spite of its minute concentration in the hydrogen, is capable when adsorbed of blocking the catalytic surface; in this case the adsorption of water should not be significantly greater than the adsorption of benzene. We would point out that the quantity of water formed from the oxygen introduced with the hydrogen in the course of the run amounted to only about 5 mole % of the benzene fed.

Another reason for the observed effect of water on the hydrogenation activity of the WS_2 catalyst might be a change in its semiconductor properties. It is well-known that water possesses both acceptor and donor properties depending on the adsorbent (see for example [4, 5]). It could be postulated that when water is adsorbed the concentration of free electrons on the catalyst surface falls, which in turn leads to a decrease in the benzene hydrogenation rate.

As regards the inhibiting effect exhibited by the presence of oxygen itself on the benzene hydrogenation process and not by the water formed from it (see above), one must suppose that the supposition of surface blocking is hardly acceptable in this case; it is highly improbable that in the conditions investigated a layer of adsorbed oxygen molecules or atoms would be maintained on the catalyst surface. The idea of the oxygen affecting the semiconductor properties of the catalyst appears to be more likely in this case. In fact oxygen is a free electron acceptor on the surface of various semiconductors and its solution in the WS_2 crystals could lead to the observed effect.

As is well-known the cracking activity of aluminosilicate catalysts increases in the presence of water. According to Gansford [7] the adsorbed water promotes the formation of carbonium ions and consequently increases the rate of reactions proceeding by an ionic mechanism. The increase in isomerization activity of the WS_2 catalyst observed by us when hydrogen with traces of water (or traces of oxygen which are converted to water on the catalyst surface) is introduced into the reaction zone may also be explained from this point of view.

The data obtained point to the fact that purification of the hydrogen from traces of oxygen and water is of great importance in the hydrogenation of benzene and the isomerization of cyclohexane over WS_2 catalyst. Purification enables the selectivity of the catalyst to be controlled and its hydrogenation activity to be raised considerably. In this connection we would point out that using hydrogen freed of traces of oxygen and water we obtained cyclohexane containing not more than 0.3% impurities from benzene over the catalyst investigated in the present study. It might be expected that the purification of the hydrogen of oxygen and oxygen-containing compounds would prove to be effective not only in the case of the hydrogenation of aromatic compounds over a WS_2 catalyst but also for the hydrogenation of other compounds over other sulfide catalysts.

E. A. Udal'tsova and Yu. I. Ryzhov took part in the work.

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THE SOLUBILITY OF POTASSIUM OZONIDE IN LIQUID AMMONIA

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It is well-known from published sources that KO_3, representative of the higher oxygen-containing compounds known as ozonides, is fairly readily soluble in liquid ammonia. This solubility has been employed in separating it from the products of the ozonization of KOH [1, 2, 4]. However the absence of quantitative data in the literature on the temperature dependence of the solubility of potassium ozonide in liquid ammonia makes it impossible to obtain KO_3 in its purest form and to separate it in the form of monocrystals. In this connection there are no references in the literature to a KO_3 purity higher than 93.3% [1] and experimental data are completely lacking on the true structure of KO_3. The authors are obliged to restrict themselves to a comparison with the similar structure of potassium azide – KN_3 [3].

Data on the Solubility of Potassium Ozonide in Liquid Ammonia

Temp., °C	KO_3 (g)/100 g NH_3	Temp., °C	KO_3 (g)/100 g NH_3
—77,7	0	—75	5,91
—78,1	1,21	—65	7,85
—78,6	2,75	—55	10,05
—79,3	3,93	—45	12,31
—80,0*	5, 1	—35	14,82

* Composition determined graphically.

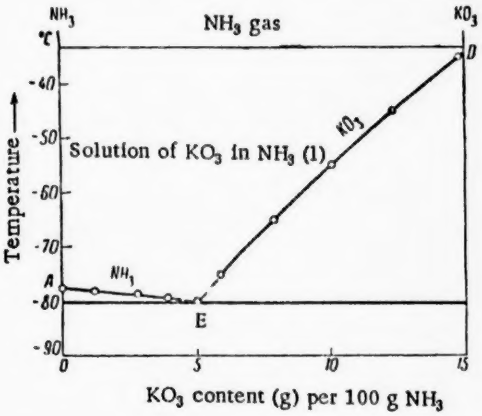

Fig. 1.

Taking all these facts into account we undertook to investigate the phase diagram of the NH_3-KOH system. In the region where KO_3 crystallizes (see the figure) the data are obtained on the basis of the isothermal solubility of potassium ozonide in liquid ammonia at temperatures of −35, −45, −55, −65 and −75°C. In the region where NH_3 crystallizes the study was carried out by the well-known visual polythermal method.

The data corresponding to the mean results of three to four measurements in the temperature range −33 to −80°, i.e., in the region where liquid ammonia is present in the stated system at ordinary pressures, are given in the table and in the NH_3-KO_3 diagram (figure).

The diagram we obtained belongs to the simplest type of eutectic diagram with a eutectic composition of about 5.1 g KO_3/100 g NH_3 at a temperature of −80°.

Elevation of the temperature leads to increased solubility of potassium ozonide in liquid ammonia with K = 0.22 g KO_3 per 1° and this reaches its maximum value near the boiling point of NH_3. According to the data obtained at −35° the solubility was found to be about 15 g KO_3/100 g NH_3. The depression of the freezing (melting) point of ammonia in the given system was from −77.7 to −80°.

The existence of the data obtained on the NH_3-KO_3 system opens up the possibility of obtaining on the one hand KO_3 in its purest form (region ED) by the method of polythermal crystallization and (on the other hand) of concentrating the dilute ozonide solutions obtained after its extraction from the ozonized alkali by the freezing out technique (region AE). Use of polythermal crystallization enabled us to obtain relatively easily separate samples of potassium ozonide with a KO_3 content equal to 98.1% by weight.

In studying the system high purity ammonia was used, prepared by triple distillation of liquid ammonia and drying with metallic sodium. The potassium ozonide was freed of the $KOH \cdot H_2O$ normally present [1] by a preliminary recrystallization and in this way its effect was reduced to a minimum. The data obtained, apart from the obvious scientific interest, may have considerable importance in the technology of potassium ozonide separation.

The experimental part will be presented in greater detail in a special paper.

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THE p-DIMETHYLAMINOPHENYL MERCURY DERIVATIVES OF NITROSOANILINES AND NITROSONAPHTHYLAMINES

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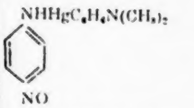
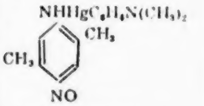
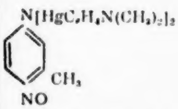
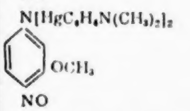
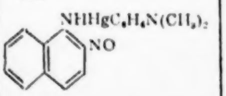
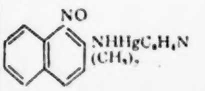
Unlike the extensively studied nitrosophenols and nitrosonaphthols the structure of nitrosoanilines and nitrosonaphthylamines has been investigated far less thoroughly. Thus there is only one reference to the fact that the absorption spectrum of p-nitrosoaniline contains a NO-group band with somewhat enhanced intensity due to the linking of the NO-group with the free pair of electrons of the amino-group [1]. This band disappears when the solution is acidified. On the basis of this fact it may be concluded that nitrosoaniline has a benzenoid structure unlike its salt which possesses a quinonoid structure, i.e., the same relationships apply here as in nitrosodialkylanilines and their salts. The Cu, Co, Ni and Pd derivatives of nitrosonaphthylamines, which find application in qualitative and quantitative analysis,were prepared, but the structure of these was not studied [2-5].

Continuing the study of the mercury aryl derivatives of tautomeric and pseudomeric systems we have investigated in the present work the reaction of p-dimethylaminophenyl mercury hydroxide with a series of nitrosoanilines and nitrosonaphthylamines which were prepared by techniques given in the literature [6-8]. The aryl mercury derivatives were synthesized in accordance with the general equation:

$$(CH_3)_2NC_6H_4HgOH + RNH_2 \rightarrow (CH_3)_2NC_6H_4HgNHR + H_2O$$

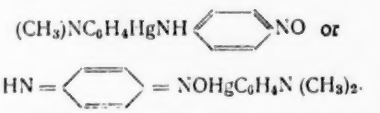
TABLE 1.

Expt. No.	Compound	Melting (decomposition) point, °C	Yield, %	C, % found	C, % calc.	H, % found	H, % calc.	N, % found	N, % calc.	Hg, % found	Hg, % calc.
1		205 from C_7H_{16} — C_5H_5N	91	37,74 37,81	38,18	3,42 3,38	3,43	9,34 9,40	9,54	45,48 45,50	45,56
2		178 from C_7H_{16} — C_5H_5N	89	41,17 41,13	40,89	4,13 4,16	4,07	8,78 8,83	8,94	42,65 42,59	42,69
3		192 from C_7H_{16} — C_5H_5N	82	35,42 35,57	35,61	3,45 3,41	3,38	7,19 7,08	7,22	51,66 51,58	51,72
4		206 from C_7H_{16} — C_5H_5N	81	34,95 35,01	34,89	3,27 3,30	3,31	6,99 7,11	7,08	50,27 50,33	50,68
5		162 from C_4H_9OH	95	43,92 43,85	43,95	3,44 3,63	3,48	8,57 8,56	8,54	40,42 40,27	40,78
6		207 from C_6H_5Cl	93	43,97 44,00	43,95	3,45 3,51	3,48	8,67 8,73	8,54	40,34 40,45	40,78

(where RNH_2 is the corresponding nitrosoaniline or nitrosonaphthylamine) by reaction of the aryl mercury hydroxide with nitrosoanilines and nitrosonaphthylamines in methanol solution (Table 1). The compounds obtained are highly colored crystalline substances, insoluble in water, very sparingly soluble in the majority of organic solvents with the exception of pyridine and melting accompanied by decomposition. The mercury aryl radical in them is not linked with the aromatic nucleus of the nitrosoaniline, which is confirmed by the following data: 1) N,N-dimethyl-substituted nitrosoanilines and dimethylaniline do not react with aryl mercury hydroxide; 2) the compounds obtained, unlike bis-p-dimethylaminophenyl mercury hydroxide, split up on reaction with potassium iodide according to the equation:

$$(CH_3)_2NC_6H_4HgNHR + KI + H_2O \rightarrow (CH_3)_2NC_6H_4HgI + RNH_2 + KOH.$$

Consequently they may have either a benzenoid or a quinonoid structure



The characteristic absorption of the NO-group was used to establish the structure of the nitrosoanilines, nitrosonaphthylamines and their aryl mercury derivatives.

TABLE 2

Expt. No.	Compound	Solvent	ν, cm$^{-1}\cdot 10^{-3}$	ϵ_{max}
1	$H_2NC_6H_4NO-4$	C_2H_5OH	15,2	53,5
2	The same	CH_3COCH_3	14,1	58,0
3	" "	$CH_3COOC_2H_5$	14,2	53,0
4	" "	C_4H_8O	15,0	57,5
5	$(CH_3)_2NC_6H_4NO-4$	C_2H_5OH	15,0	58,5
6	The same	CH_3COCH_3	14,1	60,0
7	" "	$CH_3COOC_2H_5$	14,0	57,5
8	" "	$C_4H_8O_2$	13,9	60,0
9	$H_2NC_6H_3\begin{smallmatrix}CH_3-3\\NO-4\end{smallmatrix}$	C_5H_5N	13,7	65,5
10	$(CH_3)_2NC_6H_3\begin{smallmatrix}CH_3-3\\NO-4\end{smallmatrix}$	The same	13,6	69,5
11	$(RHg)_2NC_6H_3\begin{smallmatrix}CH_3-3\\NO-4\end{smallmatrix}$	" "	14,2	90,0
12	$H_2NC_6H_3\begin{smallmatrix}OCH_3-3\\NO-4\end{smallmatrix}$	" "	13,8	78,0
13	$(CH_3)_2NC_6H_3\begin{smallmatrix}OCH_3-3\\NO-4\end{smallmatrix}$	" "	13,7	80,5
14	$(RHg)_2NC_6H_3\begin{smallmatrix}OCH_3-3\\NO-4\end{smallmatrix}$	" "	14,3	117,0
15	$H_2NC_6H_2\begin{smallmatrix}(CH_3)_2-2,5\\NO-4\end{smallmatrix}$	" "	13,7	63,5
16	$(CH_3)_2NC_6H_2\begin{smallmatrix}(CH_3)_2-2,5\\NO-4\end{smallmatrix}$	" "	13.3	47,5
17	$RHgNHC_6H_2\begin{smallmatrix}(CH_3)_2-2,5\\NO-4\end{smallmatrix}$	" "	14,0	75,0
18	$1-H_2NC_{10}H_6NO-2$	" "	14,4	80,0
19	$1-RHgNHC_{10}H_6NO-2$	" "	14,2	93,0
	$R = 4-(CH_3)_2NC_6H_4$			

To this end the absorption spectra of nitrosoanilines, nitrosonaphthylamines, their aryl mercury derivatives, and of N,N-dimethyl-substituted nitrosoanilines were obtained in the region of 10-20 cm$^{-1}\cdot 10^{-3}$ (see Figs. 1 and 2 and Table 2).* Because of the low solubility of the aryl mercury derivatives the spectra were obtained in pyridine at a cell thickness of 50-100 mm.

All nitrosoanilines and their aryl mercury derivatives possess the characteristic NO-group absorption peak in this region, which is well defined and fairly sharply separated from absorption in the UV region. Comparison of the intensity of NO-group absorption in the spectra of the N,N-dimethyl-substituted compounds with the spectra of the free compounds shows that nitrosoanilines are present in the solution entirely in the benzenoid form, unlike nitrosophenols in which the quinonoid form is predominant. The slight difference in absorption intensity is due to the effect of the substituent methyl groups. The depression of ϵ_{max} in N,N-dimethylnitrosoxylidine is probably caused by a breakdown of the association between the NO-group and the amino-group as a result of steric hindrance effects. In

* The spectra were obtained on an SFD-1 spectrometer in I. V. Obreimov's optical laboratory.

the spectra of the aryl mercury derivatives the absorption intensity at the NO-group peak is very much increased which, together with a certain amount of shift due to hypsochrome indicates the electron donor nature of the p-dimethylaminophenyl radical. It is possible that a specific solvent effect of the pyridine is manifested in this case. Thus, a comparison of absorption intensity for p-nitrosoaniline and p-nitrosodimethylaniline in different solvents indicates a significant increase in going to pyridine.

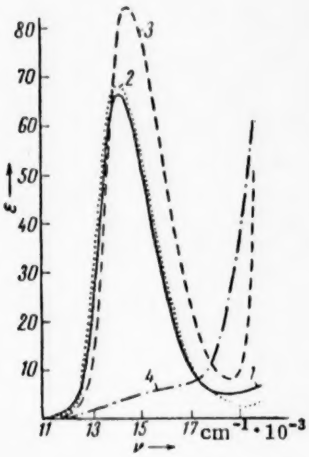
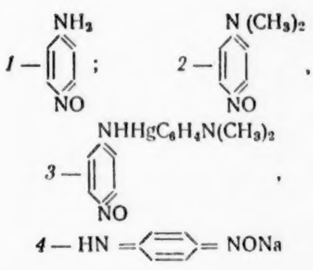


Fig. 1. Absorption spectra in C_5H_5N:



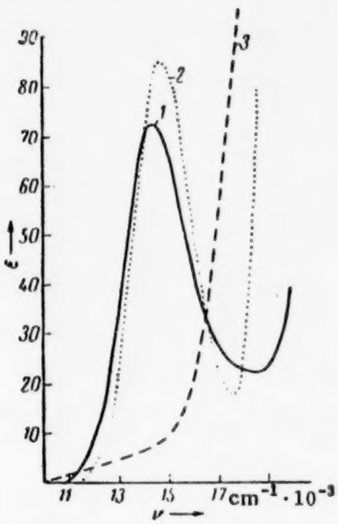
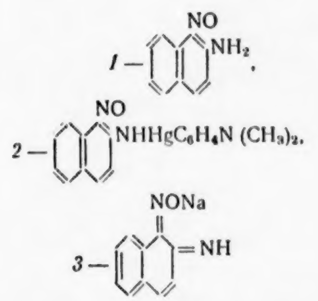
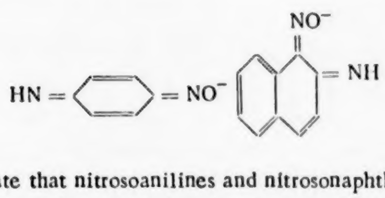


Fig. 2. Absorption spectra in C_5H_5N:



An NO-group absorption band having normal intensity is also present in the spectra of nitrosonaphthylamines and their aryl mercury derivatives, which indicates their nitrosoamine structure. In contrast with this there is no NO-group peak in the spectra of Na-derivatives of nitrosoanilines and nitrosonaphthylamines, on the basis of which we deduced a quinoidal structure for the anions of nitrosoanilines and nitrosonaphthylamines:



Thus the results obtained indicate that nitrosoanilines and nitrosonaphthylamines and also their aryl mercury derivatives have a benzenoid structure, unlike nitrosophenols, nitrosonaphthols and their aryl mercury derivatives, which primarily exist in the quinoidal form [9]. At the same time the great similarity in the behavior of the aryl mercury radical and the hydrogen atom in tautomeric and pseudomeric systems is confirmed once more.

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THE REACTION OF ACYL PEROXIDES WITH ORGANIC DERIVATIVES OF LEAD, TIN AND SILICON

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It is well-known that liquid phase reactions, in the course of which homolytic fission of σ-bonds is observed, may proceed either by way of an activated complex stage or with the formation of kinetically independent particles. In a series of cases both these mechanisms can apparently accompany each other, which is of course reflected in the variety of final reaction products. We believe that one has in fact to deal with a phenomenon of this kind in studying the reaction of benzoyl peroxide and acetylbenzoyl peroxide with heteroorganic tin compounds in the absence of solvents and atmospheric oxygen.

Since the reactions under consideration (see the table) only proceed at elevated temperatures it is logical to suppose that they are due to the breakdown of peroxide compounds:

$$C_6H_5COOOCOR \rightarrow C_6H_5COO\cdot + RCOO\cdot, \quad (1)$$
$$R = C_6H_5 \quad \text{or} \quad CH_3\cdot;$$
$$C_6H_5COO\cdot \rightarrow C_6H_5\cdot + CO_2. \quad (2)$$

From the amount of carbon dioxide evolved it is clear that reaction (2) does not play a significant role in the processes occurring in the reaction of benzoyl peroxide with tetraethyl tin, the halides of triethyl tin and the benzoates of triethyl tin (experiments 1-4).

The free benzoyl peroxide radicals formed react with the heteroorganic tin compounds. Judging by the formation of ethane ethylene and butane, this process amounts to the displacement of ethyl radicals by benzoate radicals:

$$C_6H_5COO\cdot + (C_2H_5)_3SnX \rightarrow (C_2H_5)_2SnX(OCOC_6H_5) + C_2H_5\cdot. \quad (3)$$

Here and below X = C_2H_5, Cl, Br, C_6H_5COO. Comparison of the results obtained in experiments 1-4 shows that the nature of X has little effect on the course of reaction (3). At the same time it is not possible to isolate the product $(C_2H_5)_2SnX(OCOC_6H_5)$ when X = Cl and Br. Instead of it diethyl tin dibenzoate and diethyl tin dihalide were obtained which may be explained in terms of the disproportionation of the product formed initially according to the equation:

$$2(C_2H_5)_2SnX(OCOC_6H_5) \rightarrow (C_2H_5)_2SnX_2 + (C_2H_5)_2Sn(OCOC_6H_5)_2. \quad (4)$$

The free ethyl radicals occurring in accordance with reaction (3) disproportionate and dimerize to an insignificant extent:

$$2C_2H_5\cdot \rightarrow C_2H_6 + C_2H_4, \quad (5)$$
$$2C_2H_5\cdot \rightarrow n\text{-}C_4H_{10}. \quad (6)$$

As follows from the equations given above, on decomposition of one mole of benzoyl peroxide, theoretically about two moles of mixed gaseous hydrocarbons should be formed, since reactions (2) and (6) are of a subsidiary nature.

Reaction of Benzoyl Peroxide (BP) and Acetylbenzoyl Peroxide (ABP) with Organic Derivatives of Pb, Sn, and Si in the Absence of Atmospheric Oxygen

Expt. No.	Charged to reaction, moles	Temp. °C	Duration, hours	Reaction products (1), moles per mole peroxide					
				CO_2	CH_4	C_2H_6	C_2H_4	n-C_4H_{10}	other products
1	0,010 BP 0,20 $(C_2H_5)_4Sn$	95—97	16	0,20	—	0,26	0,55	0,02	0,66 $(C_2H_5)_3Sn\ OCOC_6H_5$; 0,37 $(C_2H_5)_2\ Sn\ (OCOC_6H_5)_2$[2]
2	0,015 BP 0,15 $(C_2H_5)_3SnCl$	95—97	16	0,14	—	0,45	0,37	0,01	0,76 $(C_2H_5)_2Sn\ (OCOC_6H_5)_2$[2]; 0,63 $(C_2H_5)_2\ SnCl_2$
3	0,015 BP 0,16 $(C_2H_5)_3SnBr$	95—97	16	0,15	—	0,44	0,24	0,01	0,71 $(C_2H_5)_2Sn\ (OCOC_6H_5)_2$[3]; 0,50 $(C_2H_5)_2\ SnBr_2$
4	0,010 BP 0,044 $(C_2H_5)_3Sn\ OCOC_6H_5$	95—97	16	0,06	—	0,29	0,16	—	0,50 $(C_2H_5)_2Sn\ (OCOC_6H_5)_2$[2]; 0,29 $C_6H_5\ COOC_2H_5$
5	0,015 ABP 0,23 $(C_2H_5)_4Sn$	80—97	5,5	0,61	0,48	0,13	0,54	0,02	0,42 $(C_2H_5)_3Sn\ OCOCH_3$; 0,43 $(C_2H_5)_3Sn\ OCCO_6H_5$
6	0,010 ABP 0,16 $(C_2H_5)_3SnCl$	80—97	4	0,58	0.42	0,38	0,40	0,02	0,34 $(C_2H_5)_2Sn\ (OCOC_6H_5)_2$[2]; 0,34 $(C_2H_5)_2\ SnCl_2$[4]
7	0,005 BP 0,10 $(C_2H_5)_4Pb$	80	3,5	0,04	—	0,92	0,38	0,26	0,60 $(C_2H_5)_3\ PbOCOC_6H_5$
8	0,010 BP 0,17 $(C_2H_5)_4Si$	95—97	16	1,18	—	—	—	—	0,90 C_6H_6; 0,53 C_6H_5COOH; 0,33 $C_{16}H_{38}Si_2$[5]
9	0,0125 ABP 0,20 $(C_2H_5)_4Si$	80—97	8	1,34	0,82	—	—	—	0,78 C_6H_6; 0,23 C_6H_5COOH; 0,33 $C_{16}H_{38}\ Si_2$[6]
10	0,010 BP 0,10 $(CH_3)_3\ SnC_6H_5$	95—97	16	0,12	—	—	—	—	1,00 C_6H_6; 0,11 $C_6H_5—C_6H_5$; 1,30 $(CH_3)_3\ SnOCOC_6H_5$[7]
11	0,015 BP 0,20 $(C_2H_5)_3SiH$	95—97	16	0,63	—	0,07	0,08	traces	1,18 $C_6H_5\ COOH$; 0,60 $(C_2H_5)_3\ SiOCOC_6H_5$

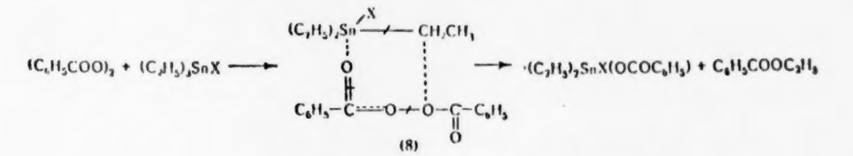
Notes: 1) Gas mixtures were analyzed by the chromatographic method; solids described above were identified by melting points and by samples mixed with the pure substances; 2) Melting point 122-124° (crystallized from hexane). Found %: C 51.80; H 5.18; Sn 27.87. $C_{18}H_{20}SnO_2$. Calculated %: C 51.59; H 4.81; Sn 28.32; 3) M. p. 122-123°. Sample mixed with diethyl tin dibenzoate obtained in experiment 2, no m. p. depression obtained; 4) on hydrolysis of the products after separation from $(C_2H_5)_3SnCl$ by distillation, CH_3COOH and 0.39 mole of $(C_2H_5)SnO$ were separated; 5) b. p. 130-134° at 3 mm; $n^{20}D$ 1.4723. Found %: C 67.09; H 12.99; Si 19.36; mol. wt. 281. $C_{16}H_{38}Si_2$. Calculated %: C 67.05; H 13.36; Si 19.58; mol. wt. 286.5; 6) b. p. 131-134° at 3 mm; $n^{20}D$ 1.4719. Found %: C 67.32; H 12.86; Si 19.20. $C_{16}H_{38}Si_2$. Calculated %: C 67.05; H 13.36; Si 19.58; 7) m. p. 129-131° (crystallized from heptane). Found %: Sn 41.32, 41.40. $C_{10}H_{14}SnO_2$. Calculated %: Sn 41.67.

It can however be seen from the table (experiments 1-4) that the over-all yield of gaseous hydrocarbons does not reach even one mole per mole of peroxide decomposed in a single case. Consequently the ethyl radicals do not only take part in the formation of gaseous substances. It is well-known for example that they can initiate the breakdown of benzoyl peroxide. In that case the ethyl ester of benzoic acid should be present in the reaction mixture:

$$C_2H_5\cdot + C_6H_5COOOCOC_6H_5 \rightarrow C_6H_5COO\cdot + [C_6H_5COOC_2H_5.] \qquad (7)$$

We isolated ethyl benzoate in fairly high yield from the products of the reaction of benzoyl peroxide with triethyl tin benzoate (experiment 4). In the remaining experiments the ethyl ester of benzoic acid could not be isolated in a pure form because of the closeness of the boiling points of this compound and the initial heteroorganic tin compounds.

Assuming a free radical scheme for the reaction, it is then easy to explain the origin of all the products found. At the same time it is admissible that ethyl benzoate is also formed in the course of the reaction, which proceeds with the formation of an intermediate activated complex. For example:



(8)

With a view of testing whether reaction (8) really occurs we investigated the reaction of acetylbenzoyl peroxide with tetraethyl tin and triethyl tin chloride (experiments 5 and 6).

As is well-known [1] acetyloxy radicals are metastable. The very fact of their existence as kinetically independent particles gives rise to some doubt. In those cases where they could be formed, one is strictly speaking dealing for practical purposes with free methyl radicals:

$$CH_3COO\cdot \rightarrow CH_3\cdot + CO_2. \qquad (9)$$

Therefore the occurrence of a significant quantity of triethyl tin acetate in experiment 5 should, in our view, be regarded as substantial proof that the reaction proceeds with the formation of an intermediate activated complex. On the other hand the presence of CO_2, CH_4 and other gaseous hydrocarbons in the reaction products points to a reaction of acetylbenzoyl peroxide with tetraethyl tin and triethyl tin chloride according to a free radical scheme.

Thus in the reaction of acyl peroxides with heteroorganic tin compounds one is apparently dealing simultaneously with both types of homolytic fission of covalent bonds.

It is possible that it is in fact this peculiarity of the process which explains why the RCOO radicals formed when the peroxides decompose predominantly attack the Sn–C bonds of heteroorganic tin compounds, whereas the methyl and phenyl radicals formed in accordance with reactions (2) and (9) split hydrogen off the ethyl groups thus being converted to methane and benzene and do not react noticeably with the tin – carbon bonds. In those cases where the reactions proceed exclusively by a free radical mechanism (for example, in the reaction of acyl peroxides with tetraethylsilane); this kind of phenomenon is not observed.

It follows from experiment 7 that the reaction of benzoyl peroxide with tetraethyl lead does not differ in principle from those reactions considered above. But it is necessary to note that it is characterized by an almost complete absence of reaction (2) and proceeds successfully in milder temperature conditions. The reactions of acyl peroxides with tetraethylsilane proceed completely differently (see experiments 8 and 9).

This is apparently explained by the stability of the silicon – carbon bond to homolytic fission. As a result, processes analogous to reactions (3) or (8) cannot be found in the case of tetraethylsilane. Judging from the absence of acetic acid in either free or combined form in the reaction mixture the reaction of tetraethylsilane with acetylbenzoyl peroxide proceeds by a free radical scheme only. It is most probable that the primary step of the reactions under consideration consists of the decomposition of the acyl peroxides according to equations (1), (2) and (9). The free radicals formed split hydrogen off the tetraethylsilane molecules with the formation of benzoic acid, benzene and methane.

Recombination of the secondary radicals with one another results in the formation of complex heteroorganic silicon compounds with two or more silicon atoms in the molecule. The complete characterization of products of this type will be given in another paper. The simplest compound of this type isolated in fairly high yield in experiments 8 and 9 is a substance with composition $C_{16}H_{38}Si_2$, similar in properties and analysis to compound (A) described earlier in the literature [2]:

$$\begin{array}{c} (C_2H_5)_3\,SiCHCH_3 \\ \quad\quad | \\ (C_2H_5)_3\,SiCHCH_3. \end{array} \tag{A}$$

The stability of the Si–C bond to homolytic fission was also discovered previously in an investigation of the decomposition of benzoyl peroxide in a trimethylphenylsilane medium [3]. It was found in this case that the benzene nucleus of trimethylphenylsilane is attacked. As a result trimethyldiphenylsilane isomers are the main silicon-containing products.

It has already been pointed out above that the reactions of analogous tin and silicon heteroorganic compounds with peroxides differ significantly form one another. Study of the reaction of benzoyl peroxide with the heteroorganic tin analog of trimethylphenylsilane therefore appeared to be of interest (experiment 10). It was established that this reaction is marked by an absence of gaseous hydrocarbons in the reaction mixture and an extremely low yield of carbon dioxide.

Consequently reaction (2) is of a subsidiar y nature, while the displacement of CH_3 radicals by benzoate radicals does not occur.

In the course of the reaction trimethyl tin benzoate is formed in high yield, the structure of which was confirmed by synthesis:

$$(CH_3)_3SnOH + C_6H_5COOH \rightarrow (CH_3)_3Sn\,OCOC_6H_5 + H_2O. \tag{10}$$

This fact justifies the statement that in the trimethylphenyl tin molecule the σ-bond situated between the benzene nucleus and the metal atom is most subject to homolytic fission. The yield of diphenyl amounts in all to 0.1 mole per mole of peroxide decomposed. This points to a lack of similarity with the processes observed in the reaction of benzoyl peroxide with trimethylsilane.

Finally, we also studied the reaction of benzoyl peroxide with triethylsilane (experiment 11). In this case the silicon-hydrogen bond is mainly subjected to homolytic fission. As a result of this,triethylsilicon benzoate is the main silicon-containing product. In addition to this, ethane, ethylene and butane are formed in extremely low yield, which is apparently explained by the occurrence of processes similar in character to reaction (3). It was not possible to detect the occurrence of dimerization of the secondary silicon-containing radicals, which is so typical of the reaction of $(C_2H_5)_4Si$ with peroxides. Research in this field continues.

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THE CATALYTIC SYNTHESIS OF 2-n-PROPYL-4-ALKYLTETRAHYDROFURANS

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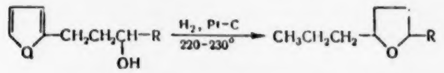
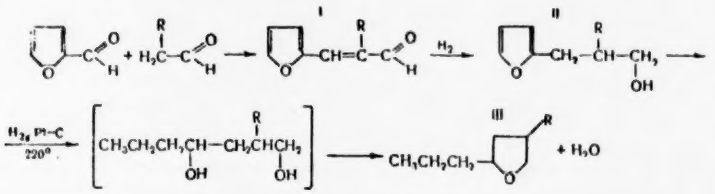
The present article discusses the catalytic synthesis of 2-n-propyl-4-alkyltetrahydrofurans from 1-furyl-2-alkylpropan-3-ols. This synthesis further broadens the new method for obtaining homologs of tetrahydrofuran from furfural and aliphatic carbonyl compounds which we discovered.

In our preceding communication [1] we described the conversion of 1-furylalkan-3-ols to 2-n-propyl-5-alkyltetrahydrofurans under hydrogenating conditions in a flow system at ordinary pressure with a platinum catalyst.



The starting compounds, 1-furylalkan-3-ols, were obtained by catalytic hydrogenation of furfurylidene ketones—the products of the condensation of furfural with aliphatic ketones.

The feasibility of synthesizing dialkyltetrahydrofurans with one alkyl group in the β-position by the condensation of furfural with aldehydes is clearly seen from the scheme:



We condensed furfural with propiono-, butyro-, and isovaleraldehydes. The α-alkyl-β-furylacroleins (I) obtained were reduced to the corresponding 1-furyl-2-alkylpropan-3-ols (II), which were subsequently converted to the 2-n-propyl-4-alkyltetrahydrofurans (III) by hydrogenation on platinized charcoal by the flow method.

Synthesis of α-alkyl-β-furylacroleins [2]. To a mixture of 700 ml of water, 300 ml of ethyl alcohol, and 10 g of sodium hydroxide, cooled to 0°, was added 95 g of furfural with occasional stirring, and, subsequently, during 4-5 hr, 1.4 moles of the aldehyde. After being mixed for 1 hr at room temperature, the reaction mixture was neutralized with acetic acid; the precipitated dark oil was washed with water and distilled under reduced pressure.

In this way were obtained α-methyl-β-furylacrolein (b. p. 92-94°/8 mm), α-ethyl-β-furylacrolein (b. p. 92-94°/6 mm), and α-isopropyl-β-furylacrolein (b. p. 89-91°/5 mm) with yields of 60-70%.

Hydrogenation of α-alkyl-β-furylacroleins to 1-furyl-2-alkylpropan-3-ols. The α-alkyl-β-furylacroleins were converted with yields of 75-85% into the corresponding 1-furyl-2-alkylpropan-3-ols by hydrogenation in the liquid phase at 120-130° over a skeletal Cu-Al catalyst. The catalyst, in the form of small lumps, was prepared by treatment of a Cu-Al alloy (30% Cu) with a 20% solution of sodium hydroxide taken in a quantity necessary for the removal of about half of the aluminum. The 1-furyl-2-alkylpropan-3-ols obtained were distilled under reduced pressure; they possessed the following properties:

1-Furyl-2-methylpropan-3-ol, b. p. 72-74°/4 mm; d^{20}_4 1.0243; $n^{20}D$ 1.4785.

1-Furyl-2-ethylpropan-3-ol, b. p. 81-82°/3 mm; d^{20}_4 1.0059; $n^{20}D$ 1.4797.

1-Furyl-2-isopropylpropan-3-ol, b. p. 98-99°/4 mm; d^{20}_4 1.0013; $n^{20}D$ 1.4846.

Conversion of 1-furyl-2-alkylpropan-3-ols into 2-n-propyl-4-alkyltetrahydrofurans. The 1-furyl-2-alkylpropan-3-ols were subjected to hydrogenation on platinized charcoal in a flowing system at ordinary pressure. The alcohols mentioned were converted into 2-n-propyl-4-alkyltetrahydrofurans by this treatment. The largest yields of the tetrahydrofurans (65-80%) were obtained at temperatures of 215-230°.

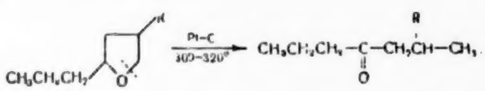
The catalyst—platinized charcoal, containing 10% platinum-was prepared by impregnation of activated charcoal with a solution of chloroplatinic acid; the latter was reduced with hydrogen in a reaction tube at 250-320°. The 2-n-propyl-4-alkyltetrahydrofurans obtained were distilled over sodium at ordinary or reduced pressure; they possessed the following properties:

2-n-Propyl-4-methyltetrahydrofuran, b. p. 148-151°/750 mm; $n^{20}D$ 1.4226; d^{20}_4 0.8463. MR_D found 38.54; $C_8H_{16}O$, calculated MR_D 38.59.

2-n-Propyl-4-ethyltetrahydrofuran, b. p. 63-65°/19 mm; $n^{20}D$ 1.4280; d^{20}_4 0.8465. MR_D found 43.23; $C_9H_{18}O$, calculated MR_D 43.21.

2-n-Propyl-4-isopropyltetrahydrofuran, b. p. 64-67°/11 mm; $n^{20}D$ 1.4316; d^{20}_4 0.8478. MR_D found 47.77; $C_{10}H_{20}O$, calculated MR_D 47.82.

Isomerization of the 2-n-propyl-4-alkyltetrahydrofurans to aliphatic ketones. Earlier we established [3] that homologs of tetrahydrofuran can be isomerized to aliphatic carbonyl compounds in the vapor phase on a platinum catalyst. We subjected the 2-n-propyl-4-alkyltetrahydrofurans to isomerization on Pt—C in the vapor phase at 300-320°. In agreement with our former data [3], it was found that 2-n-propyl-4-alkyltetrahydrofurans also are isomerized to aliphatic ketones, with yields of 80-85%:



where

$R = CH_3, C_2H_5$, iso-C_3H_7

The aliphatic ketones which were formed were separated from the reaction products by distillation of the catalyzate on a column at normal or reduced pressure. By the isomerization of 2-n-propyl-4-methyltetrahydrofuran there was obtained 2-methylheptanone-4, b. p. 154-156°; n^{20}_4 1.4108; d^{20}_4 0.8125. Semicarbazone, m. p. 123-124°. 2-n-Propyl-4-ethyltetrahydrofuran, as a result of isomerization, gave 3-methyloctanone-5, b. p. 59-60°/10 mm; $n^{20}D$ 1.4212; d^{20}_4 0.8236. Semicarbazone, m. p. 61-62°. From 2-n-propyl-4-isopropyltetrahydrofuran there was obtained 2,3-dimethyloctanone-5, b. p. 55-56°/4 mm; $n^{20}D$ 1.4285; d^{20}_4 0.8341.

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THE DIETHYL ESTER OF 1-ETHOXY-1-CYCLOHEXENE-2-PHOSPHONIC ACID

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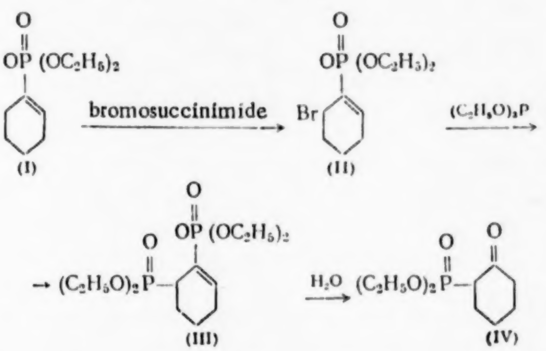
In previous communications [1] we have shown that esters of cyclohexanone-2-phosphonic acid cannot be prepared by the Arbuzov rearrangement or by the Michaelis-Becker reaction.

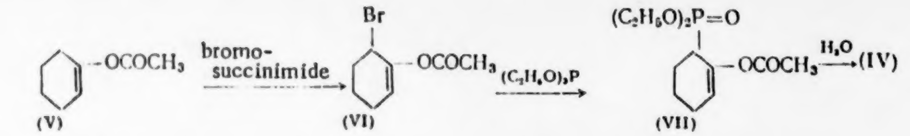
The diethyl ester of cyclohexanone-2-phosphonic acid was prepared by a circuitous route through the diethylphosphoric ester of the enol form of an ester of cyclohexanone-2-phosphonic acid (III) by transesterification of the latter compound with ethyl alcohol [2]. The comparatively low yield of the phosphoric ester of cyclohexenolphosphonic acid and the rather good reproducibility of the experiments prompted us to determine the reason for this and also to seek other routes for the synthesis of esters of cyclohexanonephosphonic acid.

The reaction between dibromocyclohexanone and triethyl phosphite, which we have previously described in a brief communication [2], is accompanied by the formation of a considerable amount of lower boiling fractions and depends to a great extent on the conditions under which the experiment is carried out. A further study of these fractions revealed that they contained diethyl phosphite, triethyl phosphate, diethyl cyclohexanone-2-phosphonate, and unsaturated compounds, which included some diolefinic compounds. One of the reasons for the complex course of the reaction may well be the effect of the conformation of the initial dibromocyclohexanone, and this possibility led us to carry out experiments to determine the action of triethyl phosphite and of sodium diethyl phosphite on cis- and trans-2,6-dibromo- and 2,6-dichlorocyclohexanones.

A possible route for the synthesis of the diethylphosphoric ester of the enol form of cyclohexanone-2-phosphonic acid ester (III) appeared to be bromination of diethylcyclohexenyl phosphate (I) with bromosuccinimide and subsequent reaction of triethyl phosphite with the resulting monobromide.



This route did not lead to the desired results. Nor did another variant, through the synthesis of diethylphosphonylcyclohexanone, lead to positive results:



The major product of this reaction proved to be the diethyl cyclohexenyl ester of phosphoric acid (I).

I. F. Lutsenko and M. Kirillov [3] have shown that the addition of phosphorus pentachloride to enol acetates can yield α-phosphonaldehydes and α-phosphonoketones.

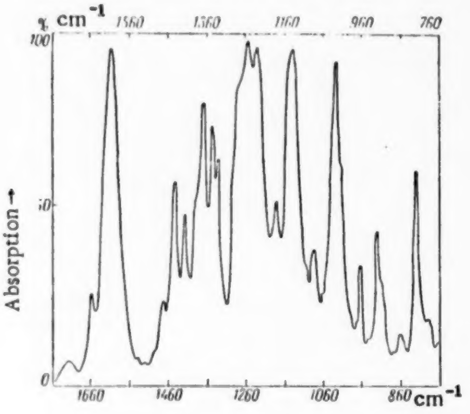


Fig. 1. I.r. spectrum of acid chloride (IX) (film).

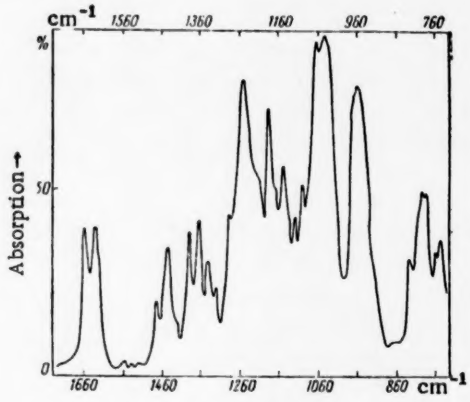
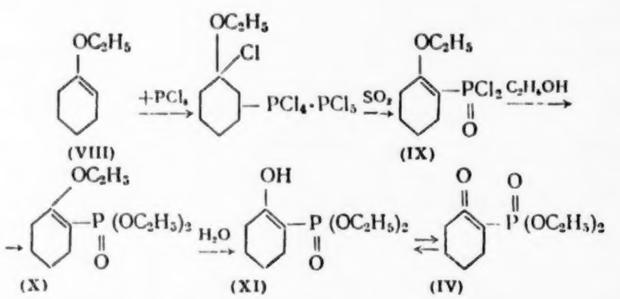


Fig. 2. I. r. spectrum of diethyl 1-ethoxy-1-cyclohexene-2-phosphonate (X) (film).

We were unable to select suitable conditions for carrying out the reaction of phosphorus pentachloride with the enol acetate of cyclohexanone. We were able to accomplish the synthesis of diethyl cyclohexanone-2-phosphonate starting with 1-ethoxycyclohexene.



The addition of phosphorus pentachloride to ethoxycyclohexene (VIII) and subsequent treatment of the complex with sulfur dioxide gave acid chloride (IX) with a b. p. of 136°/ 2 mm, d^{20}_4 1.3009, $n^{20}D$ 1.5275; MR_D found 57.52. $C_8H_{13}O_2Cl_2P$ calculated 55.43.

The Raman spectrum of acid chloride (IX) had the following frequencies (in cm^{-1}): 165 (6 b), 180 (3), 248 (5), 296 (2), 321 (3), 347 (2), 371 (2), 398 (7), 408 (2), 450 (2 db), 491 (5), 502 (2), 529 (3 b), 571 (2), 604 (0), 674 (1), 736 (1), 825 (4), 866 (3), 907 (1), 967 (3), 1016 (0), 1033 (2), 1080 (4), 1143 (2), 1181 (5), 1227 (0), 1258 (6), 1279(2), 1368 (1), 1421 (7), 1446 (4), 1456 (2), 1552 (2 b?),*, 1591 (0), 1611 (10 b),** 1662 (2), 2657 (0), 2728 (0), 2863 (5 db), 2896 (5 b), 2937 (8 b), 2979 (4).

The infrared spectrum of product (IX) (Fig. 1) had an absorption of average intensity at 1660 and a very intense one at 1611, which is characteristic of a C=C bond in a cyclohexene ring under the influence of a P=O group and

* Possibly a recurrence of the excited mercury *f* line.

** The line width was about 30 cm^{-1}.

two chlorine atoms. The broad, intense band in the region in which the P=O group absorbs had three maxima: 1272, 1255, and 1234 cm^{-1}.

Esterification of acid chloride (IX) with ethyl alcohol gave the expected diethyl 1-ethoxy-1-cyclohexene-2-phosphonate (X) with a b. p. of 122-123°/1 mm, d^{20}_0 1.0860; $n^{20}D$ 1.4735, MR_D found 67.82. $C_{12}H_{23}O_2P$, calculated 67.46.

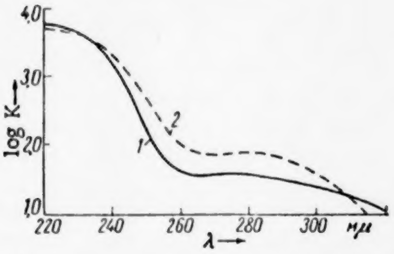


Fig. 3. U.v. absorption spectrum: 1) Diethyl 1-ethoxy-1-cyclohexene-2-phosphonate (X) in CH_3OH; 2) diethyl cyclohexanone-2-phosphonic acid in isooctane.

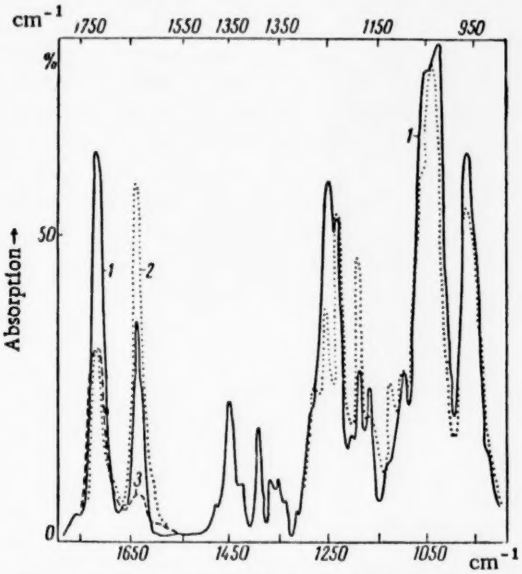


Fig. 4. I.r. spectrum of diethyl cyclohexanone-2-phosphonate: 1) Film; 2) in hexane, c ≈ 4.5 wt.%, d = 0.1 mm; 3) in iso-C_4H_9OH, c = ≈ 1 wt. %, d = 0.03 mm.

The Raman spectrum of diethyl 1-ethoxy-1-cyclohexene-2-phosphonate (X) had the following frequencies (in cm^{-1}):* 258 (2), 270 (2), 328 (1), 354 (2), 437 (1), 502 (0), 521 (0), 563 (0), 586 (0), 612 (1), 653 (0), 677 (1), 712 (1), 750 (2), 812 (2), 828 (2), 865 (2), 910 (2), 949 (1), 967 (0), 1034 (2 b), 1083 (2), 1100 (3), 1119 (2), 1149 (1), 1176 (2), 1236 (1), 1282 (2 b), 1338 (1), 1364 (2), 1388 (1), 1430 (2), 1442 (4), 1456 (3), 1480 (0), 1636 (4), 1665 (3), 2723 (0), 2843 (3), 2870 (4), 2898 (3), 2931 (6 b), 2981 (4 b), 3064 (1).

The infrared spectrum of product (X) is shown in Fig. 2. In place of the intense, broad band at 1611, which was present in the i.r. spectrum of acid chloride (IX) (Fig. 1), the i.r. spectrum of diethyl 1-ethoxy-1-cyclohexene-2-phosphonate (X) had an absorption of average intensity at 1636, which is in agreement with the 1632 frequency corresponding to the C=C bond in the enol form (XI) of diethyl cyclohexanone-2-phosphonate (see Fig. 4). There was a similar change in the frequencies of the valence vibrations of the C=C bond in the Raman spectra of products (IX) and (X).

The u.v. spectrum of diethyl 1-ethoxy-1-cyclohexene-2-phosphonate (X) (Fig. 3) also was closely similar to the u.v. absorption spectrum of diethyl cyclohexanone-2-phosphonate in isooctane, where the equilibrium is strongly shifted toward the enol form [2].

Saponification of ester (X) by aqueous acid gave the diethyl ester of cyclohexanone-2-phosphonic acid with a b. p. of 111-113°/1 mm, d^{20}_0 1.1231 $n^{20}D$ 1.4660. The constants are in complete agreement with the constants of the ester previously described by us [2].

The i.r. spectrum of this ester also was in agreement with the spectrum of the diethyl ester of cyclohexanone-2-phosphonic acid prepared by transesterification of ester (III) (Fig. 4). The i.r. spectrum of diethyl cyclohexanone-2-phosphonate, like the Raman spectrum [2], had frequencies of 1710 and 1632, which are characteristic of the keto (IV) and enol (XI) forms, respectively. The i.r. spectrum of this compound in solution in hexane retained these bands in the same positions as in the spectrum of the liquid ester, but there was a significant change in their intensity: The intensity of the band at 1710 decreased, and the intensity of the band at 1632 increased greatly. This indicates that in hexane solution there is a shift in the equilibrium toward the enol form. The considerable decrease in the intensity of the 1632 band when the ester was dissolved in isobutyl alcohol (Fig. 4, 3) was associated with a decrease in the amount of the enol form in the more polar solvent.

In the region in which the P=O group absorbs, in hexane solution the intensity of the peak at 1255 decreased, and the absorption at 1195 greatly increased. The possibility that the P=O group in the enol form takes part in the formation of an intramolecular hydrogen bond cannot be ignored.

* The spectrum had a vague background.

EXPERIMENTAL

The action of phosphorus pentachloride on ethoxycyclohexene. The ethoxycyclohexene, b. p. 55°/14 mm $n^{20}D$ 1.4589, was prepared by elimination of a molecule of ethyl alcohol from cyclohexanone acetal by heating under vacuum (170-188 mm) in the presence of camphorsulfonic acid and quinoline [5]. The acetal was prepared by the interaction of cyclohexanone with tetraethoxysilane [4].

Ethoxycyclohexene (37.6 g) dissolved in benzene was added dropwise, with stirring and cooling, to a suspension of 124.4 g of PCl_5 in 200 ml of absolute benzene. The reaction mixture was allowed to stand for two days at room temperature, and was then treated with SO_2 until the precipitate had completely dissolved. Vacuum fractionation gave the following fractions: 1) 86-92°/2.5 mm; 2) 128-136°/2 mm.

Redistillation of the higher-boiling fraction yielded 1-ethoxy-1-cyclohexene-2-phosphonyl chloride with a b. p. of 136°/2 mm, d^{20}_0 1.3009; $n^{20}D$ 1.5275. The yield was 22 g. MR_D found 57.52. $C_8H_{13}O_2Cl_2P$, calculated 55.43.

Found %: P 12.53, 12.64; Cl 29.23, 28.70. $C_8H_{13}O_2Cl_2P$. Calculated %: P 12.75; Cl 29.16.

Preparation of the diethyl ester of 1-ethoxy-1-cyclohexene-2-phosphonic acid. To a solution of 30 g of 1-ethoxy-1-cyclohexene-2-phosphonyl chloride, b. p. 136°/2 mm, in 100 ml of absolute ether was added dropwise with stirring and cooling, a mixture of 25 g of triethylamine and 17.5 ml of ethyl alcohol (20% excess). After separation of the triethylamine hydrochloride, the residual liquid was distilled under vacuum. There was obtained 16.3 g (50% of theoretical) of the diethyl ester of 1-ethoxy-1-cyclohexene-2-phosphonic acid with a b. p. of 122-123°/1 mm; d^{20}_0 1.0860; $n^{20}D$ 1.4735; MR_D found 67.82. $C_{12}H_{23}O_4P$, calculated 67.46.

Found %: P 12.32, 12.22. $C_{12}H_{23}O_4P$. Calculated %: P 11.82.

Saponification of the diethyl ester of 1-ethoxy-1-cyclohexene-2-phosphonic acid was carried out by agitating the ester with dilute HCl (1:10) in a separatory funnel. The solution was repeatedly extracted with ether. The ether extract was dried with Na_2SO_4, and the ether was distilled. Vacuum distillation of the residue yielded the diethyl ester of cyclohexanone-2-phosphonic acid with a b. p. of 111-113°/1 mm; d^{20}_0 1.1231; $n^{20}D$ 1.4660 [2].

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INVESTIGATION OF THE NATURE OF THE CHEMICAL COMPOUNDS IN THE SYSTEM Ti–Si

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(Presented by Academician I. I. Chernyaev, October 27, 1960)
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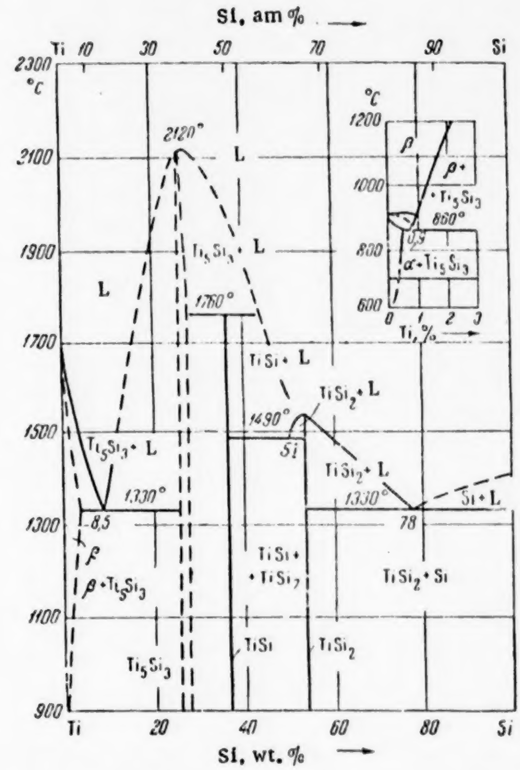
In connection with the investigation of the nature of alloys containing titanium silicide, there has arisen the necessity of studying the metallic compounds formed in alloys of the Ti–Si binary system in the region of 0.25-7.5 wt. % Si. The broadest investigation of the equilibrium diagram of the titanium–silicon system was carried out by Hansen and co-workers [1], who used x-ray analysis to show the existence of metallic compounds which were also detected in this system by an organometallic method [2]. According to the statements of these authors, the phase which they discovered contained 37.5-40 atom % silicon. Pietrokowsky and Duwez [3] consider that the crystalline structure of this phase corresponds to the formula developed on the basis of the chemical composition. This compound has a hexagonal structure isomorphous with the compounds Mn_5Si_3, Fe_5Si_3, Ti_5Sn_3, and Ti_5Ge_3 [2].



The present work comprised an investigation of the nature of the metallic compounds in alloys of titanium with small amounts of silicon (0.25-7.5 wt. % Si).* The investigation was carried out by electrolytic precipitation

* The alloys used in this investigation were prepared and kindly presented to us by E. N. Pylaeva.

of the compounds at the anode. The literature contains no description of electrolytes suitable for anodic solution and isolation of titanium silicides from alloys on the titanium side of the system.

The alloys used in the investigation were fused, annealed at 1000° for 24 hr, and quenched in water or annealed at 500° for 500 hr and quenched in water in conformity with the equilibrium diagram.

The new electrolyte which we proposed for the anodic separation of the $TiCr_2$ phase from titanium–chromium alloys [4] proved to be suitable for isolating the intermetallide phase from the Ti–Si alloy containing 7.5 wt.% Si. This electrolyte has the composition: 3 ml H_2SO_4 (1.84), 3 g succinic acid, and 1000 ml methanol.

The presence of the above phase was confirmed by chemical and x-ray analysis in all experiments carried out with that particular alloy. This phase is titanium silicide, Ti_5Si_3, and the composition is strictly stoichiometric in conformity with the chemical formula. However, with the other Ti–Si alloys investigated, which contained small amounts of silicon – 0.25, 0.50, 0.75, 1.0, and 2.0% – it was not possible to separate titanium silicide by anodic solution in this electrolyte.

In this connection, we proposed a new electrolyte having the composition 15 ml H_2SO_4 (1.84), 3 g ascorbic acid, and 1000 ml of methyl alcohol [5]. Using this electrolyte, we found it possible to carry out anodic solution of alloys on the titanium-rich side of the Ti–Si system and containing small amounts of silicon; at the same time, titanium silicide of precisely the composition Ti_5Si_3 with a weight ratio of Ti to Si of 2.85 and an atom ratio of 1.68 was separated.

TABLE 1. Results of the Microchemical Analysis of the Anode Powders. Electrolyte: 15 ml H_2SO_4 (1.84), 3 g Ascorbic Acid, 1000 ml Methyl Alcohol. (Experiment time, 1.5 hr. Current density, 0.05 amp/sq cm)

Si content of charge, wt. %	Found in anode powder, wt.%		Ti + Si, wt. %	Ti : Si by wt.	Found, atom. %		Ti + Si, atom.%	Ti : Si (atom)	Composition of compound	X-ray analytical results
	Ti	Si			Ti	Si				
0,25	No powder separated									
0,50 *	72,66	27,18	99,84	2,70	61,05	39,35	100,40	1,60	Ti_3Si_3	Ti_5Si_3
0,50 *	74,99	24,78	99,77	2,82	62,32	37,67	99,99	1,66	same	—
0,75 *	74,02	26,30	100,32	2,81	62,25	37,75	100,00	1,65	» »	Ti_5Si_3
75 *	75,00	25,16	100,16	2,97	63,90	36,10	100,00	1,77	» »	
1,00	75,95	23,71	99,66	2,74	65,25	34,73	99,98	1,67	» »	
2,00 *	74,85	25,00	99,85	2,99	63,50	36,93	100,40	1,71	» »	
2,00 *	74,95	25,04	99,99	2,99	63,68	36,32	100,00	1,75	» »	
7,50 *	74,00	26,32	100,32	2,87	63,12	36,86	99,98	1,71	» »	Ti_5Si_3
7,50 *	75,00	25,00	100,00	3,00	64,48	35,50	99,98	1,80	» »	

* Electrolyte contained 3 ml H_2SO_4 (1.84), 3 g ascorbic acid, and 1000 ml methyl alcohol.

TABLE 2. Effect of Current Density on Composition and Yield of Phase. Electrolyte: 1000 ml Methyl Alcohol, 15 ml H_2SO_4 (1.84), 3 g Ascorbic Acid. (Alloy investigated contained 7.5% Si; experiment time, 1.5 hr)

Current density, amp/sq cm	Yield of phase, wt. %	Found, wt. %				Found, atom %			
		Ti	Si	Ti+Si	Ti : Si	Ti	Si	Ti+Si	Ti : Si
0,03	12,09	75,20	24,54	99,74	3,05	64,23	35,76	99,99	1,79
0,05	11,36	75,06	24,64	99,70	3,04	64,11	35,88	99,99	1,78

Table 1 presents the results of microchemical analyses of the anode powders from Ti–Si alloys. After anodic solution of the sample, the separate powder was washed by centrifuging with water and then with alcohol and dried under a stream of hydrogen in a quartz tube on an oil bath. The dried material was analyzed by microchemical and x-ray methods.*

* The x-ray analysis was carried out by M. A. Volkova.

We also investigated the effect of current density on the composition and yield of the phase, and we found that the optimum current density lies within the range of 0.03 to 0.05 amp/sq cm (Table 2).

At a current density of 0.1 amp/sq cm, there was considerable evolution of heat. Replacement of the complex former ascorbic acid by sulfosalicylic acid also gave an electrolyte suitable for the separation of the strictly stoichiometric titanium silicide phase (Table 3).

TABLE 3. Results of Microchemical Analyses of Anode Powders. Electrolyte: 1000 ml Methyl Alcohol, 15 ml H_2SO_4 (1.84), 3 g Sulfosalicylic Acid. (Current density, 0.05 amp/sq cm; experiment time, 1.5 hr)

Si content of alloy, wt. %	Yield of phase, wt. %	Found, wt. %				Found, atom %			
		Ti	Si	Ti+Si	Ti : Si	Ti	Si	Ti+Si	Ti : Si
0,50	12,90	74,83	25,04	99,87	2,98	63,62	36,36	99,98	1,74
0,75	12,14	74,70	24,94	99,64	2,99	63,68	36,32	100,00	1,75
2,00	13,32	74,67	25,08	99,76	2,88	63,59	36,41	99,99	1,74

A material balance of the electrolysis products was carried out with respect to the decrease in weight of the anode, and the following good results were obtained (in grams): Weight of dry anode powder, 0.0742; 0.0363 Ti and 0.0043 Si found in powder; 0.04840 Ti and 0.0105 Si found in electrolyte after separation of phase; 0.6093 total; loss in anode weight, 0.6144.

Method of Microchemical Analysis

A sample of the dried anode powder weighing 0.01 g (weighed on a microbalance) was placed in a platinum crucible and fused with an accurately weighed 5 g portion of potassium persulfate, which was added in two doses. After fusion of the first portion of the salt, the crucible was cooled, the second portion of persulfate was added, and the crucible was again heated in a muffle furnace. The cooled fused mass was leached with water containing 10 ml of H_2SO_4 (1.84), and the solution was twice evaporated to the evolution of dense white vapors.

The precipitated silicic acid was removed by filtration, washed with 5% (by volume) of warm HCl to a negative reaction for iron salts (tested with a crystal of potassium ferrocyanide). The filtrate was retained for determination of titanium. The washed precipitate was placed in a platinum crucible, dried, combusted in a muffle furnace at 1000°, and weighed.

This material was wetted with 1-3 drops of H_2SO_4 (1:1) and 2 ml of HF was added. The mixture was carefully evaporated to dryness and calcined, and, after the crucible had cooled, it was weighed. The difference between the first and second weighings was taken as the amount of silicic acid.

A blank sample was carried through all stages of the analysis. The titanium determination was carried out in the filtrate from the silicon separation by a colorimetric method utilizing hydrogen peroxide.

The compound Ti_5Si_3 was found by both the microchemical and the x-ray method of analysis in all of the Ti–Si alloys investigated.

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A QUANTITATIVE EVALUATION OF THE EFFECT OF SUBSTITUENTS ON THE POLAROGRAPHIC REDUCTION OF CERTAIN AZOMETHINE COMPOUNDS

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One of the most pressing problems of present day chemistry is the establishment of a quantitative relationship between the structure of organic compounds and their reactivity. In the general case, this problem is still very complex; however, individual rules described by empirical or semiempirical equations are entirely practicable, and they make it possible to express numerically the effect of the structure of a molecule on the reactivity of the compound. First and foremost, this applies to the Hammett rule, which encompasses the rate constants and equilibrium constants of nucleophilic substitutions of aromatic compounds with substituents in the para or meta positions [1-3]. Since polarographic reduction of a functional group can be considered as a nucleophilic substitution reaction, then, as has been shown by a number of authors [4-7], the Hammett equation for an electrochemical reaction assumes the following form: $E_{\frac{1}{2}} - E^0_{\frac{1}{2}} = \rho'\sigma$, where $E^0_{\frac{1}{2}}$ and $E_{\frac{1}{2}}$ are, respectively, the half-wave potentials of the unsubstituted and substituted derivatives, ρ' is a constant of the electrochemical reaction characterizing the susceptibility of the reacting center (the group undergoing reduction) to the effect of the substituent, and σ is a constant characterizing the extent of the effect of a given substituent in the benzene ring on the ability to undergo reduction. Whether the Hammett equation can justifiably be applied to irreversible reactions, in particular to irreversible polarographic reduction, can be determined only by obtaining data on a series of derivatives under completely equivalent conditions.

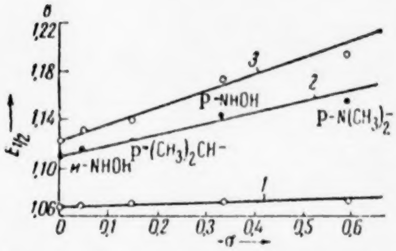
In polarography, the Hammett rule has been found to apply not only for aromatic compounds (tropolone, benzaldehyde, acetophenone, benzophenone, nitro compounds, azobenzene, phthalimide) [4-8], but also for heterocyclic [9-10] (thiophene, selenophene, pyrrole, furan, pyridine, thiazole, tetrazolium salts), quinoid [7], and pseudoaromatic [11] (azulene, sydnone) compounds. There are various possibilities of applying the Hammett rule to polarographic reactions of organic compounds. In the first place, such application would permit prediction of the polarographic behavior of one derivative from the values determined for others; in the second place, it could be used for the identification of compounds in mixtures, including isomers, for the determination of equilibrium constants when ρ' is known [12], and for the quantitative evaluation of the effect of substituents on the electrode process.

With the aim of evaluating quantitatively the effect of substituents on the reduction of compounds containing an azomethine group, we have applied the Hammett equation to the polarographic reduction of phenylhydrazones and semi- and thiosemicarbazones of some aromatic aldehydes. Such derivatives of benzaldehyde, p-isopropylbenzaldehyde, p-dimethylaminobenzaldehyde, and p- and m-nitrobenzaldehydes were studied along with derivatives of acetophenone and p-chloroacetophenone. The polarographic study of these compounds was carried out in 20% methanol—water solutions with a concentration of 10^{-4} mole/liter; the supporting electrolyte was phosphate—borate buffer with a pH of 6.0; the temperature was 25°. Table 1 presents the results of a microcoulometric and polarographic investigation of some of the azomethine derivatives mentioned above. These results show that both phenylhydrazones and semi- and thiosemicarbazones are reduced by the same mechanism.

It was also found that four electrons take part in the reduction of the nitro group in derivatives of p- and m-nitrobenzaldehydes; i.e., the nitro group in these compounds is reduced to a hydroxylamine group. Therefore, we have examined the effect of a hydroxylamine group, rather than a nitro group, on the polarographic reduction of the

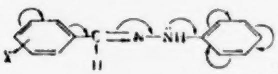
$\gt C = N -$ bond in derivatives of the nitrobenzaldehydes.

Using the values of the half-wave potentials shown in Table 2, we constructed a graph showing the variation in $E_{\frac{1}{2}}$ with σ (in Hammett's units) [2]. As may be seen from Fig. 1, the linear relationship between half-wave potential and values of σ was satisfactory for the compounds studied. The values ρ' shown in Table 3 were determined from the slopes of these lines. The value of ρ' for semicarbazones of aromatic aldehydes is close to the value 0.12-0.13 found by Pearson for semicarbazones of certain benzophenones [4]. Our values of ρ' are relatively small, i.e., the effect of the substituents on the reduction of the azomethine group in the compounds studied is comparatively insignificant, and the extent of this effect, which depends on the natures of the bonds in the molecule through which the electronic effect is propagated, increases in the series phenylhydrazone, thiosemicarbazone, semicarbazone.



1) Phenylhydrazones; 2) thiosemicarbazones; 3) semicarbazones.

The electronic structures of all the compounds investigated are characterized by $\pi p \pi$-conjugation and by a relatively high lability of the overall electron cloud of the molecule, the density of which is most uniform in the case of the phenylhydrazones:

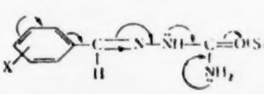


This is due to the presence of a second phenyl radical at the end of the conjugated chain. Since the reducible azomethine bond occurs not at the end of the conjugated chain but merely as one of the transmitting units of this chain, its electron density changes insignificantly under the effect of one substituent or another in the benzene ring of the original aldehyde. This explains the rather close values of the half-wave potentials of derivatives of substituted and unsubstituted carbonyl compounds.

TABLE 1.

Expt. No.	Azomethine derivative	No. of electrons taking part in reduction	Slope of line $E = f\,(\log \frac{i}{id - i})$	$\frac{dE_{\frac{1}{2}}}{d\,pH}$
1	Benzaldehyde phenylhydrazone	1.80	0.048	0.050
2	Acetophenone phenylhydrazone	1.94	0.062	0.038
3	Acetophenone semicarbazone	1.90	0.070	0.043
4	Benzaldehyde thiosemicarbazone	1.97	0.056	0.055
5	Acetophenone thiosemicarbazone	2.09	0.060	0.033

Semi- and thiosemicarbazones, in contrast to phenylhydrazones, have an electronegative oxygen or sulfur atom at the end of the conjugated chain, and the direction of the action of these atoms on the molecules agrees with the direction of polarization of the $\rangle C = N-$ bond and with the effect of electron-donor substituents in the benzene ring; they also cause a shift in the overall electron cloud in their direction.



This shift is more significant in semicarbazones, since the more electronegative oxygen atom, as compared to the sulfur atom, causes greater asymmetry of the electron cloud of the conjugated bonds on the molecule and a greater effect on the electron density of the azomethine group.

Thus, the effect of substituents appears to a greater extent in semicarbazones than in thiosemicarbazones and phenylhydrazones.

TABLE 2.

Expt. No.	Carbonyl compound	Half-wave potential, in volts relative to n.c.e.		
		phenylhydrazone	thiosemicarbazone	semicarbazone
1	Benzaldehyde	−1.065	−1.110	−1.122
2	p-Isopropylbenzaldehyde	−1.068	−1.123	−1.138
3	p-Dimethylaminobenzaldehyde	−1.070	−1.150	−1.190
4	p-Nitrobenzaldehyde	−1.070	−1.144	−1.174
5	m-Nitrobenzaldehyde	−1.068	−1.115	−1.130
6	Acetophenone	−1.170	−1.210	−1.276
7	p-Chloroacetophenone	−1.154	−1.162	−1.220

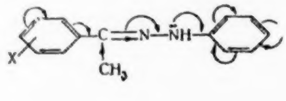
TABLE 3.

Expt. No.	Carbonyl compound	ρ'-Constant for reduction of $>C=N'$ bond		
		phenylhydrazones	thiosemicarbazones	semicarbazones
1	Aromatic aldehydes	0.004	0.094	0.132
2	Acetophenones	0.070	0.208	0.244

TABLE 4.

Expt. No.	Substituent	$-E_{1/2}$, B		σ	
		para	meta	para	meta
1	—	−0,480		0	
2	$-\underset{H}{\underset{\mid}{C}}=N-NH-C_6H_5$	0,340	0,356	+0,88	+0,78
3	$-\underset{H}{\underset{\mid}{C}}=N-NH-\underset{S}{\underset{\|}{C}}-NH_2$	0,350	0,378	+0,81	+0,64
4	$-\underset{H}{\underset{\mid}{C}}=N-NH-\underset{O}{\underset{\|}{C}}-NH_2$	0,350	0,373	+0,81	+0,67

The somewhat higher values of ρ' for azomethine derivatives of acetophenones can be explained by the effect of the methyl radical, which disrupts the relatively uniform density of the electron cloud of the system of conjugated bonds and increases the electron density of the azomethine group.



Therefore, the electron density at $>C=N-$ bonds can easily change under the influence of substituents in the benzene ring. In the case of p-chloroacetophenone derivatives, the electronegative chlorine atom acts in a direction opposite to the direction of polarization of the azomethine bond and leads to a decrease in the electron density there; i.e., it facilitates polarographic reduction.

The nitrobenzaldehyde azomethine derivatives studied in this work can be considered as substituted aromatic nitro compounds. Therefore, these data allow us to solve the reverse problem – that of calculating values of σ for phenylhydrazone and semi- and thiosemicarbazone substituents by electrochemical reduction of the nitro group. Table 4 presents values of σ of these substituents calculated from the difference in half-wave potentials of the substituted and unsubstituted nitrobenzenes on the assumption that $\rho' = 0.16$ [5, 8].

The values of σ calculated for the different substituents containing an azomethine group proved to be very close, i.e., these groups exert a similar effect on reduction of a nitro group, the effect being transmitted through the system of π-bonds of the benzene ring. This also indicates a similarity in the electronic structures of these substituents with that of a $\pi p \pi$-conjugated system of bonds, which possesses a relatively high lability of the over-all electron cloud.

In conclusion, it should be pointed out that the values of ρ' and σ presented in the present work are approximate, since they were obtained by a study of a small number of compounds; they undoubtedly require refinement.

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A METHOD OF CLEAVING TOLUENE-C^{14} TO DETERMINE THE POSITION OF THE LABEL IN THE RING

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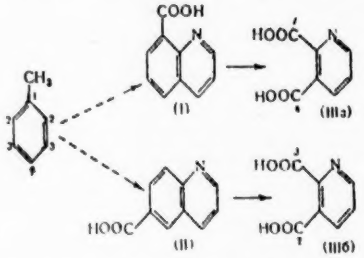
In studies of isomerization of aromatic compounds, shifting of the migrating group is usually determined with respect to another substituent present in the same molecule. Thus, the mechanism by which an alkyl group in benzene derivatives migrates has been studied by investigating the isomerization of dialkylbenzenes, particularly xylenes. It must be kept in mind, however, that the presence of a second substituent in the aromatic molecule can have an effect on the nature and direction of shift of the migrating group, and, therefore, considerable care must be exercized in considering conclusions as to mechanism on the basis of such investigations.

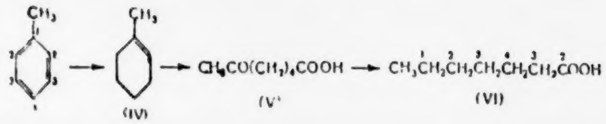
For these reasons, in investigations of isomerization processes it would seem desirable to determine the route by which the migrating group shifts by reference to one of the ring positions which is labeled with radioactive carbon C^{14} rather than relative to a second substituent. We have used this method to study the mechanisms of migration of substituents (Cl, CH_3, HO_3S) in naphthalene derivatives [1-3]. However, it is not possible unconditionally to extend the theoretical conclusions formed during the course of this work to the isomerization of compounds of the benzene series, since the naphthalene ring differs from the benzene ring by a significant localization of the double bonds [4]. This stimulated us to enter into a study of the isomerization of monosubstituted benzenes labeled with radiocarbon. The first compound studied was toluene-1-C^{14}, which is currently available commercially [5].

In order to carry out this investigation, it was necessary to develop a method of cleaving toluene-C^{14} which would allow us to carry out separate determinations of the radioactivity of each atom of the benzene ring. After this part of the work had been completed, a communication by Dutch investigators was published [6] describing a method of cleaving toluene-C^{14}. This original method was based on conversion of the toluene by nitration and oxidation to a mixture of nitrobenzoic acids. The individual o- and p-nitrobenzoic acids were separated from this mixture, reduced to the corresponding aminobenzoic acids, and then converted by the Skraup reaction to the isomeric quinolinecarboxylic acids (I and II). Oxidation of the latter and stepwise decarboxylation of the resulting quinolinic acids (IIIa and IIIb) permitted determination of each atom of the benzene ring in the form of carbon dioxide:



The accuracy of the results obtained in a determination of the distribution of radiocarbon in a benzene ring by means of this method depends on complete separation of the nitrobenzoic acids and on the selectivity of the decarboxylation of the quinolinic acids.

The data of B. A. Kazanskii and N. F. Glushnev, which show that upon reduction by $Ca(NH_3)_6$ toluene is converted predominantly to 1-methylcyclohexene (IV) [7] (see also [8-10]), was used in our proposed method. The 1-methylcyclohexene is further oxidized with permanganate [11], and the resulting keto acid (V) is reduced to enanthic acid (VI):



Successive removal of carbon atoms from the enanthic acid molecule is easily accomplished by means of methods described in the literature [12, 13]. We used the following scheme for this purpose:

$$\underset{}{RCH_2COOH} \rightarrow \underset{(VII)}{HCH_2COC_6H_5} \rightarrow \underset{\underset{NOH}{\|}}{RCCOC_6H_5}\,(VIII) \rightarrow RCN + C_6H_5COOH$$

$$RCN\,(IX) \downarrow \quad \underset{(X)}{RCONH_2} \rightarrow \underset{(XI)}{RCOOH}$$

The aliphatic acid was converted through the acid chloride to the alkyl phenyl ketone (VII) by Friedel-Crafts reaction, and the α-isonitroso derivative (VIII) of the ketone was converted by the Beckmann II rearrangement under the influence of concentrated sulfuric acid to the nitrile (see [13]). The resulting nitrile (IX) hydrolyzed under the reaction conditions to amide (X), which was isolated and, after purification, subjected to further hydrolysis to aliphatic acid (XI), which contained one less carbon atom than the original acid. Further shortening of the chain of this acid was obtained by repeating this series of operations. The carbon atom removed from the molecule of aliphatic acid was fixed in the carboxyl group of the benzoic acid. Measurement of the radioactivity of samples of this acid obtained during the course of the cleavage allowed us to determine the distribution of radiocarbon in the molecule of toluene-C^{14}.

The proposed method of cleavage is suitable for other alkylbenzenes labeled with radiocarbon.

It is difficult to say at the present time which of these two methods of cleavage of toluene-C^{14} is the more convenient. It will be possible to answer this question only after actual use of both of them for the determination of the position of radiocarbon in the isomerization products of alkylbenzenes -C^{14}.

EXPERIMENTAL

Reduction of the toluene. To a 300 ml Favorskii flask was charged 20 g of metallic calcium turnings, and a stream of dry ammonia (dried with solid potassium hydroxide) was passed through a tube extending to the bottom of the flask until there was no further absorption of the ammonia. The increase in weight comprised 80-85% of the amount calculated for $Ca(NH_3)_6$. The toluene, 12 g, was added from a dropping funnel over a period of 0.5 hr to the solid porous mass of $Ca(NH_3)_6$, and the mixture was allowed to stand for two days at room temperature. When the contents of the flask were subsequently heated on a molten metal bath to 300°, a colorless liquid distilled, the i.r. spectrum of which was identical to the spectrum of 1-methylcyclohexene prepared from cyclohexanone by the method of reference [14]. The yield of 1-methylcyclohexene from reduction of the toluene was 45-50%.

When, as recommended in reference [7], half the amount of calcium was used for the reduction, i.e., 2 gram atoms per mole of toluene, the reduction product (80% yield) contained a significant amount of toluene (see also [8-10]).

δ-Acetyl-n-valeric acid (V). To a three-neck flask, fitted with a thermometer and stirrer, was charged 4.4 g of 1-methylcyclohexene, obtained by reduction of toluene, and 110 ml of water. Then, with vigorous stirring, 17.8 g of finely ground potassium permanganate was added over a period of 6 hr, during which time the reaction mixture was cooled to maintain a temperature of 0-2°; the reaction mixture was then allowed to stand overnight at room temperature. The precipitated manganese dioxide was removed by filtration and washed with 100 ml of hot water. The combined filtrate was extracted with ether, 150 g of ammonium sulfate was dissolved in it, and the solution was made acid with hydrochloric acid. The precipitated keto acid was extracted with ether and converted by the usual method [15] to the semicarbazone. The yield was 4.0 g (64%); m. p. 110-125°. Recrystallization from water gave 2.4 g with an m. p. of 141.5-142.5°. According to reference [16], the m. p. of δ-acetyl-n-valeric acid semicarbazone is 144°.

Enanthic acid (VI). A 1.5 g sample of the semicarbazone was heated with 1.8 g of potassium hydroxide in 9 ml of diethylene glycol at a bath temperature of 200° for 15 hr. The mixture was poured into water and neutralized with 15% hydrochloric acid, and the separated enanthic acid was extracted with ether. The yield was about 100%. The

i.r. spectrum of this acid was completely identical to the spectrum of commercial enanthic acid; their S-benzylthiuronium salts were also identical – m. p. 145.0-145.5°.

Found %: N 9.53, 9.70. $C_{15}H_{24}N_2O_2S$. Calculated %: N 9.46.

Cleavage of the enanthic acid was carried out by the method of reference [13] through enanthophenone (80% yield) and α-isonitrosoenanthophenone (32% yield); the cleavage yielded caproic acid (80% yield) and benzoic acid. The caproamide was hydrolyzed to free acid, and the cycle was repeated.

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A RADIATION-KINETIC METHOD FOR THE DETERMINATION OF ULTRASMALL AMOUNTS OF POLONIUM*

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(Presented by Academician I. V. Tananaev, November 16, 1960)
Translated from Doklady Akademii Nauk SSSR, Vol. 137, No. 4, pp. 869-872, April, 1961
Original article submitted November 14, 1960

The ability of periodide ions to give intense solid-phase color reactions [1] and the lesser ability of iodide ions to do this can be used for the photometric determination of very small amounts of tetravalent polonium (Po^{210}).

This is accomplished through a combination of several processes: The coprecipitation of the polonium, the resulting local acceleration of radiolysis of the iodides, the formation of periodide anions, and the solid-phase color reaction of these anions with butylrhodamine cations.** It is possible to select such conditions of iodides and butylrhodamine that the solid-phase color reaction caused by the formation of a suspension of butylrhodamine iodide will take place only to an insignificant extent. However, it will take place to some extent, and, in accordance with the rule for coprecipitation by organic precipitants [2], tetravalent polonium will be deposited as butylrhodamine penta- or hexapolonite on the butylrhodamine iodide crystals [3]. This local increase in polonium concentration on the butylrhodamine iodide crystals causes an increase in the local radiolysis of iodide ions, which leads to the formation of elemental iodine and, further, periodide. The latter brings about the conversion of new amounts of butylrhodamine into the insoluble state and thereby an increase in the solid-phase color reaction caused by the formation of small crystals of butylrhodamine periodide. These small crystals cause coprecipitation of additional amounts of polonium, and the process is repeated; the process is, therefore, autoaccelerating.

It is important that the local increase in polonium concentration is accompanied by a simultaneous local increase in the concentration of periodide in the crystals of butylrhodamine periodide. As a consequence of this, radiolysis takes place to a greater extent in the resulting heterogeneous system than in a homogeneous system of the same composition. As may be seen from the material presented later in this paper, this is important with regard to the sensitivity and, in particular, the selectivity of the reaction. Owing to this, it is possible to determine polonium in the presence of preponderant amounts of certain other alpha emitters.

Selectivity of the reaction. This solid-phase color reaction with butylrhodamine can be given by all those elements which, under the conditions of the reaction, are present in solution in the form of hydrophobic complex anions. Among these are both elements which form iodine-containing anions (Te^{IV}, Cd, Hg, Bi, Sb, etc.) and elements which may be present in the form of other complex anions, for example, oxygen-containing anions. But this reaction will be the ordinary, simple, nonautoaccelerating solid-phase color reaction. These same elements can also be coprecipitated with butylrhodamine iodide.

If radioactive isotopes of any of the coprecipitating elements are present and the radiation from these isotopes causes appreciable radiolysis of iodides, then these elements will give the same autoaccelerating color reaction as polonium. The sensitivity of the reaction will be determined by the intensity of the radiolysis.

Sensitivity of the reaction. The sensitivity of the reaction is greater, the greater the time allowed for the occurrence of radiolysis, the higher the concentration of the iodide solution in which the reaction is carried out, and the

* The analytical reaction described in this article is based on an autoaccelerating process. At the Conference on Kinetic Methods of Analysis (June 14-16, 1960 at Ivanovo), at which the present work was reported, a name for this new type of analytical reaction was discussed. In a practical regard and with respect to its high sensitivity, this new reaction is closely similar to catalytic reactions, but is not such in the strict sense of the term. Perhaps, this autoaccelerating reaction should be called an "avalanche" or a "radiation-avalanche" reaction.

** The n-butyl ester of rhodamine B. The synthesis was carried out by L. I. Bol'shakova.

higher the concentration of butylrhodamine. But if the concentrations of the components exceed certain rather small limits, a blank test begins to give a positive reaction as a consequence of the formation of a suspension of small crystals of butylrhodamine.

The reliability of the reaction decreases with an increase in the iodide concentration owing to the conversion of iodide to periodide under the influence of atmospheric oxygen, light, and hydrogen peroxide formed as a result of radiolysis. Radiolysis in the solution is greatly increased by the presence of other radioactive elements. Thus, the sensitivity of the reaction and the magnitude of the correction as determined by a blank experiment increase in parallel under the influence of the same factors.

Substances which combine with elemental iodine may be introduced to provide greater reliability of the reaction. These substances should be introduced in a concentration selected to ensure a sufficiently small correction as measured by the blank experiment. Resorcin is a suitable substance. On the contrary, in order to increase the sensitivity of the reaction it is desirable to add to the system a small amount of elemental iodine in a concentration such that the resulting periodide will give an appreciable, but not a strong positive reaction. In this case, small crystals of butylrhodamine periodide will be present in the system immediately after the introduction of the components, and the coprecipitation of polonium on them begins immediately. Periodide is always present in some concentration in the ordinary yellowish solution of potassium iodide which has not been freshly prepared, and such a solution of potassium iodide gives a very sensitive reaction. Table 1 shows the effect of the above factors on the sensitivity of the reaction. The following concentrations were used: Polonium (Po^{210}) $2.5 \cdot 10^{-5}$ γ/ml; KI $9.6 \cdot 10^{-3}$ M, butylrhodamine chloride, $5.5 \cdot 10^{-5}$ M. The activity of the solution was $1.1 \cdot 10^{-6}$ scin/liter.* The temperature was 20°. The measurements were made three minutes after the introduction of the components.

TABLE 1. Effect of the Presence of Elemental Iodine on the Sensitivity of the Reaction in 4.0 N H_2SO_4

Expt. No.	Introduced: resorcin (moles)	Introduced: iodine (moles)	Color intensity in nominal scale units: blank	expt. with polonium	difference in nominal scale units	Nonimal sensitivity, γ/ml polonium*
1	$2{,}9 \cdot 10^{-1}$	—	1	1	0	
2	$1{,}7 \cdot 10^{-1}$	—	1	1	0	
3	$1{,}5 \cdot 10^{-1}$	—	1	1	0	
4	$8{,}7 \cdot 10^{-2}$	—	1	1	0	
5	$5{,}8 \cdot 10^{-2}$	—	1	1	0	
6	$2{,}9 \cdot 10^{-2}$	—	1	3	2	$1{,}2 \cdot 10^{-7}$
7	—	—	1	3	2	$1{,}2 \cdot 10^{-7}$
8	—	$6{,}4 \cdot 10^{-6}$	1	3	2	$1{,}2 \cdot 10^{-7}$
9	—	$1{,}1 \cdot 10^{-5}$	1	3	2	$1{,}2 \cdot 10^{-7}$
10	—	$2{,}1 \cdot 10^{-5}$	1	4	3	$8{,}3 \cdot 10^{-8}$
11	—	$6{,}3 \cdot 10^{-5}$	1	4	3	$8{,}3 \cdot 10^{-8}$
12	—	$1{,}1 \cdot 10^{-4}$	1	4	3	$8{,}3 \cdot 10^{-8}$
13	—	$2{,}1 \cdot 10^{-4}$	1	6	5	$5{,}0 \cdot 10^{-8}$

* Calculated polonium concentration causing a color intensity equal to one nominal scale unit.

The experiments for which results are shown in Table 1 were carried out in tubes with visual evaluation against a comparison scale. This scale, which was merely a collection of colored solutions with a smoothly changing color from rose to violet-blue, was prepared as follows:

Tube No.	1	2	3	4	5	6	7	8	9	10
a	:	1,8	1,6	1,4	1,2	1,0	0,8	0,6	0,4	0,2
b	0	0,2	0,4	0,6	0,8	1,0	1,2	1,4	1,6	1,8
c	0,015	0,055	0,103	0,148	0,198	0,250	0,300	0,363	0,425	0,468

Note: a) 0.001% aqueous solution of safranine; b) 0.0014% aqueous solution of methylene blue; c) extinction compared to water. FĚK-M yellow filter; 5 mm cell.

* The polonium concentration was determined by the scintillation method [5]. The error in the measurement did not exceed ± 5%.

It is easily seen that at a polonium concentration of $2.5 \cdot 10^{-7}$ γ/ml a quite distinct positive reaction was obtained after three minutes reaction time. Under the conditions of Expt. 13, Table 1, the extinction of the solution in excess of that of the blank was 0.235. One-fifth to one-seventh of this extinction, which corresponds to a polonium concentration of about $5 \cdot 10^{-8}$ γ/ml, can be confidently determined with an ordinary photocolorimeter. These data relate to the isotope Po^{210}, an alpha emitter with a half-life of 138 days. The sensitivity of the reaction will be different, of course, for other isotopes.

Such high sensitivity is rare, even among the very highly sensitive catalytic reactions. It should be emphasized that this very high sensitivity is not limited; the sensitivity can be increased by increasing the time allowed for the reaction to take place or by the introduction of larger amounts of iodine.

Method. We describe here a method suitable for the sensitive determination of polonium (Po^{210}) in pure solutions and one for the determination of polonium in the presence of plutonium 239. The solution must not contain the elements indicated above, which give a solid-phase color reaction with butylrhodamine.

Before carrying out the reaction, it is necessary to prepare the solution, ensuring the presence of polonium in the form of suitable ions and the removal from the polonium solution of hydrogen iodide, which constantly accumulates due to radiolysis [4, 6]. The hydrochloric or nitric acid solution of polonium was evaporated to dryness, H_2SO_4 was added, and the mixture was heated to the appearance of sulfur trioxide vapors; the mixture was then cooled and diluted with water to a concentration of 6 N H_2SO_4.

Determination of polonium in pure solutions. To 1.3 ml of the resulting solution with an acidity of 6N with respect to H_2SO_4 was added 0.37 ml of a freshly prepared 1% solution of potassium iodide and 0.1 ml of an 0.01% aqueous solution of elemental iodine, and the mixture was maintained in the darkness at 20° for 20 minutes. Next, 0.32 ml of an 0.02% aqueous solution of butylrhodamine chloride was added, and, after 5 minutes, the color was evaluated visually against the standard scale or by a photometric method. The polonium content was determined from a calibration curve, which was constructed in the same manner, using solutions of known polonium concentration.

Determination of polonium in the presence of plutonium. This determination was carried out in the same manner except that the calibration curve was constructed for solutions containing approximately the same amount of plutonium as the solution being investigated.

If the amount of plutonium in the latter is not known, it is necessary to construct a number of calibration curves for solutions. All of the components except the butylrhodamine were added to an aliquot of the solution being analyzed, and the mixture was held in the dark for 25 minutes. The butylrhodamine was then introduced, and the light absorption was determined immediately. This value was considered as the light absorption of a blank test. The calibration curve selected was one for which the solution without polonium had a light absorption as close as possible to the value obtained for the blank sample.

TABLE 2. Photometric Determination of Polonium by Means of a Radiation-Kinetic Solid-Phase Color Reaction. Volume of the Final Solution, 2.1 ml

Taken in γ		Po/Pu	Po^{210} found	Error, in %	Taken, in γ		Po/Pu	Po^{210} found	Error, in %
Po^{210}	Pu^{239}				Po^{210}	Pu^{239}			
$1{,}1 \cdot 10^{-7}$	—	—	$8{,}0 \cdot 10^{-8}$	−27	$5{,}0 \cdot 10^{-9}$	—	—	$6{,}9 \cdot 10^{-9}$	+40
$8{,}3 \cdot 10^{-8}$	—	—	$7{,}1 \cdot 10^{-8}$	−24	$1{,}1 \cdot 10^{-7}$	$9{,}8 \cdot 10^{-4}$	1:99000	$1{,}0 \cdot 10^{-7}$	−8
$7{,}3 \cdot 10^{-8}$	—	—	$6{,}4 \cdot 10^{-8}$	−12	$2{,}2 \cdot 10^{-8}$	$9{,}8 \cdot 10^{-4}$	1:45000	$2{,}3 \cdot 10^{-8}$	+4
$6{,}2 \cdot 10^{-8}$	—	—	$6{,}3 \cdot 10^{-8}$	+1	$1{,}7 \cdot 10^{-8}$	$9{,}8 \cdot 10^{-4}$	1:58000	$1{,}8 \cdot 10^{-8}$	+6
$5{,}6 \cdot 10^{-8}$	—	—	$5{,}5 \cdot 10^{-8}$	−2	$1{,}1 \cdot 10^{-8}$	$9{,}8 \cdot 10^{-4}$	1:89000	$1{,}4 \cdot 10^{-8}$	+27
$9{,}9 \cdot 10^{-9}$	—	—	$6{,}2 \cdot 10^{-9}$	−37	$8{,}6 \cdot 10^{-9}$	$9{,}8 \cdot 10^{-4}$	1:114000	$1{,}1 \cdot 10^{-8}$	+27
$8{,}3 \cdot 10^{-9}$	—	—	$7{,}6 \cdot 10^{-9}$	−8					

Table 2 presents examples of results obtained in determinations of polonium in pure solutions and in solutions containing tetravalent plutonium (Pu^{239}). In the last experiment, in which the polonium concentration was $8.6 \cdot 10^{-9}$ γ and the plutonium concentration was $9.8 \cdot 10^{-4}$ γ, the activity of the plutonium present with respect to alpha decompositions per unit time was 1.6 times the activity of the polonium.

The mechanism discussed earlier can be used to create highly sensitive radiation-kinetic reactions for other elements which have isotopes possessing rather high alpha activity and which yield ions which can be coprecipitated with organic coprecipitants.

In accordance with the mechanism iodide → periodide, this is possible for all elements which form complex iodide anions. In accordance with the mechanism nitrate → nitrate → nitrogen compound, this is possible for elements which form stable complex nitrate anions. In accordance with the mechanism perchlorate → chlorate → readily oxidizable organic products, this is possible for elements which can be coprecipitated with organic perchlorates, i.e., elements which can form ions of the form MeO_4^-. These and other combinations will be considered in detail in future publications.

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ON THE INTERACTION OF NITROBENZENEDIAZONIUM FLUOBORATE WITH PHOSPHORUS TRICHLORIDE

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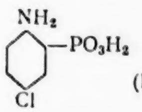
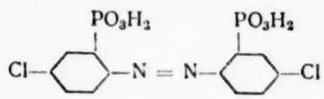
While both m- and p-nitrobenzenephosphonic acids can be synthesized by the diazo method of Doak and Freedman without any particular difficulty [1-3], the ortho isomer cannot be prepared by this route [4]. Our experiments have confirmed these data. At the same time, in an investigation of a reaction mixture formed in a corresponding manner, which we assumed to contain o-nitrobenzenephosphonic acid, we unexpectedly found a compound which could be diazotized. From this diazo compound (without separation) we were able to obtain (by coupling with 1-naphthalene-4-sulfonic acid) an azo compound which, upon investigation, proved to be a mixture of two azo dyes — one a product of coupling of the naphthalenesulfonic acid with chloroaniline and the other an amine containing a chloro and a phosphono group. With the aim of isolating this amine (i.e., chloroaminobenzenephosphonic acid), we decided to attempt to use the ability, which we assumed it had, to give a difficultly soluble complex with heavy metals, the formation of which should dictate an ortho distribution of the phosphono and amino groups. As a matter of fact, it was possible to isolate such a complex with copper, and decomposition of the complex gave chemically pure 2-aminochlorobenzenephosphonic acid (I).

The position of the chlorine in (I) was established by showing the 2-hydroxychlorobenzenephosphonic acid obtained from (I) by replacement of the amino group by a hydroxyl to be identical to 2-hydroxy-5-chlorobenzenephosphonic acid obtained by separation from its potassium salt. A mixture of these two compounds melted without depression of the melting point.

A search for conditions promoting the formation and separation of this amine revealed that it is necessary to increase the amount of phosphorus trichloride by a factor of 3.5 and to increase the amount of copper by a factor of 5 from the amounts recommended by Doak and Freedman [4c].

An increase in the amount of copper, which was done initially for the purpose of facilitating separation of the amine, proved to have a simultaneous effect on the end result of the reaction.

At a mole-to-atom ratio of o-nitrobenzenediazonium fluoborate to copper of 1 : 1 (and a ratio to PCl_3 of 1 : 3.5), the amine was obtained in a yield of 15% (5% in the form of a dye), while at a ratio of 1 : 0.2, the amount of amine decreased appreciably (to 5%). However, under the latter condition there was a 12-15% yield of another substance which, by an investigation of its properties and composition, was shown to be azo compound (II).

 (I),  (II)

The correctness of formula (II) was confirmed not only by analysis, but also by the fact that reduction of the substance gave 2-amino-5-chlorobenzenephosphonic acid.

The formation of a small amount of nitrophenol and also chloroaniline [which was separated in the form of a salt of acid (I)] was established for all reaction conditions.

Further investigation showed that under conditions similar to those used for the synthesis of (I), chlorination and the formation of amines take place in the case of isomers of (I): i.e., the reaction is a general one, although

the extent to which it takes place differs. It must be remarked that separation through the copper complex in the manner described above was possible only for the ortho isomer; the meta and para isomers still have not been isolated as such, and have been prepared only in the form of azo dyes with resorcinol.

Dependence of the Yield of Amine on the Ratio of Diazonium Fluoborate and of Nitrobenzene to Phosphorus Trichloride (in moles)

Compound	Yield of amine, %		Degree of chlorination, %
	1:1	1:3.5	
o-Nitrobenzenediazonium fluoborate	Traces	15	100
p-Nitrobenzenediazonium fluoborate	2-2.5	30-35	15-20
m-Nitrobenzenediazonium fluoborate	Traces	10-15	15-20
Nitrobenzene	None found	2-5	0

Additional experiments with nitrobenzene showed that it is possible to form a certain amount of aniline, i.e., in this case reduction of the nitro group occurs, although the yield of reduction product is small.

Thus, we are the first to show that depending on the ratios of reactants and the so-called "catalyst," the interaction between nitrobenzenediazonium fluoborates and phosphorus trichloride can take place simultaneously in three interrelated directions: 1) the formation of a phosphono group, 2) the reduction of the nitro group, and 3) chlorination.

The last reaction is most complete with the ortho isomer.

EXPERIMENTAL*

To a mixture of 635 ml of absolute ethyl acetate, 155 ml (1.75 moles) of phosphorus trichloride, and 25 g of cuprous chloride was added, in small portions at 30°, a mixture of 118.5 g (0.5 mole) of the diazonium fluoborate and 25 g of cuprous chloride; with the addition, the temperature increased and the evolution of nitrogen began. Care was taken to ensure that the temperature did not exceed 60°. After the evolution of nitrogen ceased, the mixture was maintained at this same temperature for 3 hr. The reaction mixture was then cooled to 15-35°, 10 ml of water was carefully added, and the mixture was heated at 50-65° for 1 hr. Then, 590 ml of water was added at a temperature not above 45-60°.

In the case of the ortho isomer, the reaction mixture was neutralized with sodium carbonate to a pH of 4-5 and heated to 45°. The mixture was then cooled, and the precipitated copper complex was separated by filtration. The water layer of the filtrate was separated, and an additional amount of copper complex was obtained from it by precipitation with ethyl acetate. The precipitates were combined, washed with water, and dried at 100°. There was obtained 32 g of a substance with a greenish color. This substance was dissolved in dilute hydrochloric acid (1: 2), the copper was precipitated with hydrogen sulfide, and the resulting copper sulfide was removed by filtration. Carbon was added to the filtrate, and the filtrate was evaporated in the presence of the carbon (to half its original volume). The carbon was then filtered off, and the filtrate was neutralized with sodium carbonate to a pH of 3. The neutralization caused the formation of a white amorphous precipitate, which was separated by filtration and washed with ice water (about 75 ml).

The material was dried at 120°. There was obtained 11 g of the white amorphous substance. An analysis for sodium was negative.

Found %: P 15.02, 14.97; Cl 17.04, 17.02; N 7.01, 7.08. $C_6H_7O_3NPCl$. Calculated %: P 14.92; Cl 17.06; N 6.75.

An additional amount of chloro-o-aminobenzenephosphonic acid was separated from the filtrate in the form of an azo dye with resorcinol; the amount was 7.3 g.

* With the participation of G. B. Zavarikhina and G. P. Stepanova.

In the case of the meta and para isomers, the ethyl acetate was distilled, the copper was precipitated with hydrogen sulfide, and the copper sulfide was filtered off. The filtrate was boiled with carbon until the odor of hydrogen sulfide was gone, and was then filtered and neutralized with sodium bicarbonate to a pH of about 3-4.

The resulting solution was diazotized and poured into a soda solution of resorcinol. The resulting dye was separated by acidification with hydrochloric acid and was twice reprecipitated from water. It was dried at 70-80°. The weight of material obtained from the meta and para isomers was 11.8 and 28.4 g, respectively. In both cases the dye contained neither sodium nor chlorine ions. Analysis showed that both were mixtures of two azo compounds, one of which (obtained in considerably smaller amount) contained chlorine in the molecule; it was not possible to separate them.

Substance from the meta isomer: Found %: P 9.57, 9.67; Cl 2.1, 2.15. Substance from the para isomer: P 10.33, 10.48; Cl 2.4, 2.1. $C_{12}H_{11}O_5N_2P$. Calculated %: P 10.57. $C_{12}H_{10}O_5N_2PCl$. Calculated %: P 9.40; Cl 10.78.

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ON THE MECHANISM OF THE REACTION OF SILICON HYDRIDES WITH ORGANIC HALIDES IN THE GAS PHASE

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A number of investigators [1-13] have shown that the reaction between silicon hydrides and organic halides in the gas phase at a temperature of 500-700° and atmospheric pressure is a new general method for the preparation of aryl- and alkenylhalosilanes. Investigation of the reaction has shown that it proceeds almost quantitatively according to the equation:

$$R_nCl_{3-n}SiH + R'Cl \rightarrow R_nCl_{3-n}SiR' + R_nCl_{4-n}Si + R'H + HCl.$$

The material balance of the reaction was investigated in the present work with the aim of clarifying the mechanism of the reaction. A mixture of chlorobenzene and trichlorosilane was passed through a reactor at 580°C with a residence time of 32 seconds in the reaction zone. The kettle residue amounted to 1.7 g and contained a small amount of biphenyl; the loss was 3.0 g.

TABLE 1

Reaction	Starting compounds		Compounds obtained					
	C_6H_5Cl	$HSiCl_3$	HCl	$C_6H_5SiCl_3$	$SiCl_4$	C_6H_6	$HSiCl_3$	C_6H_5Cl
I	771 / 86,8	278 / 37,7	130 / 4,7	132 / 28,1	59,0 / 10,1	55,5 / 4,3	66,8 / 9,1	565 / 63,5
	C_6H_5Cl	CH_3SiHCl_2	HCl	$C_6H_5SiCl_2CH_3$	CH_3SiCl_3	C_6H_6	CH_3SiHCl_2	C_6H_5Cl
II	556 / 62,6	278 / 31,9	74,8 / 2,72	76,5 / 14,6	78,2 / 11,7	74,4 / 5,76	94,7 / 10,9	369 / 41,5
	$CH_3C_6H_4Cl$	$HSiCl_3$	HCl	$CH_3C_6H_4SiCl_3$	$SiCl_4$	$CH_3C_6H_5$	$HSiCl_3$	$CH_3C_6H_4Cl$
III	556 / 70,4	278 / 37,7	124,2 / 4,5	125 / 28,2	48 / 8,2	46,4 / 4,27	83,8 / 11,2	359,2 / 45,5

Note: The figures above the line give the amount of substance in millimoles; those below the line represent grams.

A study of the material balance of the reaction between chlorobenzene and trichlorosilane (I), between o-chlorotoluene and trichlorosilane (II), and between chlorobenzene and methyldichlorosilane (III) led to the following results (see Table 1). The gaseous products of the reaction amounted to 1-2% of the weight of the reactants. It is apparent from the data that the molar amounts of the hydrogen chloride and organochlorosilane formed, on the one hand, and the silicon tetrachloride (or methyltrichlorosilane) and the corresponding hydrocarbon, on the other,

were about the same. It is natural to assume that each of these pairs of compounds is formed by a separate reaction. The somewhat increased amount of silicon tetrachloride (or methyltrichlorosilane) over that of the corresponding hydrocarbon may be explained by slight pyrolysis of the trichlorosilane (or methyldichlorosilane):

$$4Cl_3SiH \rightarrow 3SiCl_4 + Si + 2H_2.$$

There is theoretical basis for the assumption that the above pairs of compounds are formed as the result of secondary reactions and not from the original compounds; for example, the following secondary may be proposed for the interaction of chlorobenzene and trichlorosilane:

$$C_6H_5SiCl_3 + HCl \rightarrow C_6H_6 + SiCl_4$$

or

$$C_6H_6 + SiCl_4 \rightarrow C_6H_5SiCl_3 + HCl.$$

Special experiments showed that neither of these reactions takes place under the conditions studied. Moreover, it was found that at a given temperature and a given ratio of reactants, the ratio of one of the above pairs of compounds to the other was practically constant.

These data persuasively indicate that the interaction between silicon hydrides and organic halides in the gas phase at atmospheric pressure proceeds by two parallel routes. For example, for chlorobenzene and trichlorosilane:

$$C_6H_5Cl + HSiCl_3 - \begin{cases} \rightarrow C_6H_5SiCl_3 + HCl & \text{(I)} \\ \rightarrow C_6H_6 + SiCl_4 & \text{(II)} \end{cases}$$

We shall designate reaction I as a condensation reaction and reaction II as a reduction reaction.

The ratio of one of these reactions to the other depends decisively on the nature of both the organic chloride and the silicon hydride. We therefore studied the reaction of trichlorosilane with various organic halides and determined in each case the ratio (in moles) of condensation products to reduction products. We denote this ratio by C/R. The condensation products were characterized by the amount of organotrichlorosilane in moles; the reduction products were characterized by the amount of silicon tetrachloride. The experimental data are presented in Table 2.

TABLE 2. Dependence of the Ratio of Condensation Products to Reduction. Products on the Structure of the Organic Halide in the Reaction with Trichlorosilane at 580°, τ = 27-30 seconds, RHal: $HSiCl_3$ = 2:1

Organic halide	C/R	Organic halide	C/R
C_6H_5Cl	2,4	$CH_2=CHCl$	17,0
p-$CH_3C_6H_4Cl$	4,2	$Cl_2C=CCl_2$	1,9
o-$CH_3C_6H_4Cl$	2,6	$CH_2=CH-CH_2Cl$	6,7
2,5-$(CH_3)_2C_6H_3Cl$	3,6	C_6H_5Br	0,1
2,4,6-$(CH_3)_3C_6H_2Cl$	3,2	α-$C_{10}H_7Br$	1,1
p-ClC_6H_4Cl	1,9	C_6H_5F	1,0
α-$C_{10}H_7Cl$	6,2	$C_6H_5CH_2Cl$	0
β-$C_{10}H_7Cl$	9,7	CH_3Cl	0
o-$C_6H_5C_6H_4Cl$	0,7	CCl_4	0

A consideration of the data of Table 2 reveals that the ratio C/R is affected by two factors — the nature of the substituent and steric hindrance. Steric hindrance — specifically, the presence of a substituent ortho to the chlorine atom attacked — decreased the value of C/R. This conclusion follows from a comparison of the values of C/R for α- and β-chloronaphthalenes. The introduction of electron donor substituents into the aromatic ring increased the value of C/R. It is interesting that in the case of 2,4,6-trimethylchlorobenzene, the value of C/R was higher than that for orthotolyl chloride in spite of the presence of methyl groups in both positions ortho to the chlorine atom. The introduction of electron acceptor substituents brought about a decrease in C/R. The value of C/R was several times higher for the chloronaphthalenes than for the benzene derivatives and was approximately the same order as

C/R for allyl chloride. The highest value of C/R was obtained with vinyl chloride. Practically no reaction occured by the reduction scheme in the case of the aliphatic chlorides, and C/R = 0.

TABLE 3. Dependence of the Ratio of Condensation Products to Reduction Products on the Structure of the Silicon Hydride in the Reaction with Chlorobenzene at 540°, τ = 28 seconds. $C_6H_5Cl : R^1R^2R^3SiH = 2:1$

Silicon hydride	C/R	Silicon hydride	C/R
Cl_3SiH	2.4	$C_6H_5SiCl_2H$	1.1
CH_3SiCL_2H	1.0	$(C_6H_5)_3SiH$	0.1
$C_2H_5SiCl_2H$			

The nature of the halogen in the organic halide also has a considerable effect on the value of C/R. The replacement of chlorine by both bromine and fluorine led to a decrease in C/R. Further investigation showed that the nature of the second component of the reaction also had a considerable effect on the value of C/R. The data of Table 3 show that replacement of a chlorine atom in trichlorosilane by an alkyl or aryl radical brought about a relative increase in the reduction reaction. The extent of reaction by the reduction scheme was greater, the greater the number of chlorine atoms replaced by radicals.

That this reaction is homolytic in nature has previously been shown [1, 3, 4], and there is evidently no cause to doubt this conclusion. The data obtained in the present work have extended our knowledge of the mechanism of this reaction, and they introduced some new aspects.

The production of radicals evidently occurs by thermal dissociation of Si–H bonds, for example:

$$HSiCl_3 \rightarrow \dot{H} + \dot{S}iCl_3.$$

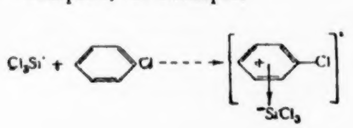
We shall consider the case of the reaction of trichlorosilane with chlorobenzene. It is improbable that the reaction is initiated by the decomposition of a molecule of the organic chloride, in which the C–Cl bond energy is significantly higher. The ease with which the silicon hydride molecules decompose leads to a constant generation of radicals. In addition, the development of chains must play a significant part in the generation of radicals. Only the $SiCl_3$ radical is regenerated during chain transfer, since the action of any other radical on a molecule of the silicon hydride, the concentration of which is relatively high, must remove a hydrogen atom with the liberation of a silyl radical. Thus, the silyl radical is the active principle during the development of the process. Evidently, both of the parallel reactions take place as a result of an attack by the silyl radical on the molecule of organic halide, but the site of the attack is different in the two cases.

In the attack of the $SiCl_3$ radical on the chlorine atom of the chlorobenzene molecule, the chlorine atom is removed, and silicon tetrachloride and a phenyl radical are formed; the latter, reacting with trichlorosilane, again yields a $SiCl_3$ radical:

$$C_6H_5Cl + \dot{S}iCl_3 \rightarrow SiCl_4 + C_6\dot{H}_5,$$
$$C_6\dot{H}_5 + HSiCl_3 \rightarrow C_6H_6 + \dot{S}iCl_3.$$

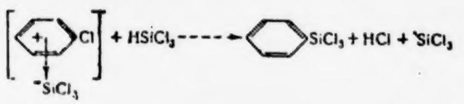
Such is the scheme of the reduction reaction. The isolation of biphenyl from the kettle residue indicates the formation of C_6H_5 during the course of the reaction, since the biphenyl is obviously formed by recombination of two phenyl radicals.

For the condensation reaction to take place, it is necessary that the C–Cl bond in the organic halide be at a carbon atom which is bonded to the neighboring carbon by a π-bond. An attack of a silyl radical on such a bond can take place with the formation of a π-complex, for example:



The formation of intermediate σ-complexes can be excluded, since reactions with the various aryl chlorides never led to the formation of isomers; moreover, the amount of gaseous reaction products was very small for such a high temperature (about 1%), which indicates the absence of disturbance of the aromatic system.

The aryltrichlorosilane and hydrogen chloride are formed and the silyl radical is regenerated during the collision of the intermediate π-complex with the trichlorosilane molecule:



Thus, in essence the mechanism of condensation and of reduction comes down to concurrent attacks of silyl radicals on the chlorine atom and on the π-electron bond of the organic halide molecule. The proposed hypothetical mechanism for the condensation and reduction reactions readily explains our experimental data, in particular: The increase in C/R when electron donor substituents are present in the chlorobenzene and the decrease in C/R when electron acceptor substituents are present; the increase in C/R in the reactions with the chloronaphthalenes; the occurrence of only the reduction reaction with saturated aliphatic chlorides, etc.

The experimental method has been described previously [1].

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APPLICATION OF NEUTRON ACTIVATION ANALYSIS TO THE DETERMINATION OF TUNGSTEN IN MINERALS AND CONCENTRATES

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Nuclear reactions and the artificial radioactivity induced by them have found application for the determination of the contents of different elements in minerals and concentrates. The nuclear reactions used for the determination of elements are those in which the yield of secondary particles depends on the element being determined [1] or those in which the yield of secondary particles for the given element is higher than that for other associated elements [2]. The artificial radioactivity used for the determination of elements in minerals and concentrates is created by a stream of neutrons (in the determination of aluminum, manganese, indium, and vanadium) [3] or by alpha particles (in the determination of aluminum and boron) [4].

We have found that induced radioactivity produced by neutrons may be used for the determination of the tungsten content of minerals and concentrates. That it is possible to use neutron activation analysis for the determination of tungsten in minerals and concentrates is due to the fact that tungsten has greater cross-section for neutron capture, which results in the production of artificial radioactivity. Tungsten has a cross-section for the reaction (n,γ) of 9.9 barns [5]. This reaction results in the formation of the radioactive tungsten isotope W^{187} ($T_{\frac{1}{2}}$ 24.1 hr). Processing of scheelite ores to concentrate the tungsten,yields concentrates in which the concentration of scheelite reaches tens of percents.

Other elements usually associated with tungsten in scheelite ores either have cross-sections for the (n,γ) reaction which are small in comparison to that of tungsten (silicon, tin, calcium, iron, sulfur, magnesium, nickel) or are encountered in amounts which do not interfere with the determination of tungsten (copper, arsenic, manganese, phosphorus).

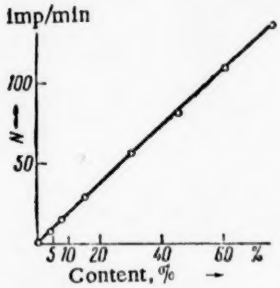
The neutron irradiation was carried out with a polonium–beryllium source in which the polonium had an activity of 8 C. The neutrons were slowed by means of a paraffin block, which contained the polonium–beryllium source at its center. Shielding from the neutrons was provided by paraffin bricks containing boron and by sheet cadmium. Lead served as shielding from the relatively weak gamma radiation of the paraffin block.

The cell containing the scheelite concentrate was activated by placing it in the center of the paraffin block, in which an appropriately located channel had been left. Counting of the induced radioactivity was carried out on the beta radiation of the β-isotope with an end window counter and a B-2 apparatus. The activation time, 1.5 hr, was selected from a consideration of the time required to obtain sufficient activity in the sample. Longer times than this caused activation of the minerals associated with the scheelite in the ore, thereby increasing the activity of the sample. The sample was kept under the counter for 20 min to decrease the activity of the light elements (aluminum, silicon).

We have determined which elements can interfere with the tungsten determination and the amounts required for interference. Radiation from elements such as manganese, molybdenum, and copper can be filtered out by means of low-energy beta ray (1.33 mev for W^{187}) filters, the activity of the sample being counted twice.

The figure shows a calibration curve for the determination of scheelite in mixtures with fluorspar. The graph, which plots the radioactivity count as a function of tungsten content, is linear, which makes it possible to determine scheelite in concentrates.

The half-life of the tungsten isotope W^{187} is relatively high; therefore, the accuracy of the determination can be increased by increasing the time during which the induced radioactivity is counted. Thus, with a counting time of 30 min, the error in the determination of scheelite in a concentrate is 1.5%. The accuracy may be increased and the time for a determination of scheelite in concentrates and ores may be decreased by increasing the activity of the polonium–beryllium source and also by increasing the diameter of the window in the end window counter. When neutron activation analysis is used for the determination of the major component in minerals and concentrates, the difficulty of chemically separting the associated elements disappears.



Dependence of induced radioactivity on the tungsten trioxide content in a mixture of scheelite and fluorspar.

The determination of the tungsten content of minerals containing manganese (huebnerite), which has a high activation cross-section with respect to thermal neutron capture, can be carried out by means of gamma radiation using the methods of nuclear spectroscopy.

In the case of ferberite, the iron has a cross-section of 0.001 barn for the (n,γ) reaction; therefore, there will be practically no activation when a polonium source having an activity of 8 C is used.

The molybdenum content of molybdenum-containing scheelite ore concentrates reaches 4.5%. An increase in the activity of the sample due to activation of the molybdenum can be avoided by holding the sample under the counter for 1.5-2 hr, since Mo^{101} which is formed in the activation, has a half-life of 14 minutes.

Neutron activation analysis can be used for the determination of the tungsten content of steels [5] and solid metal-ceramic alloys containing cobalt and titanium, the induced activity of which can be decreased by holding the sample under the counter for one-and-a-half hours.

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ON THE FORMATION OF SOLID SOLUTIONS BETWEEN TRICALCIUM AND TRISTRONTIUM SILICATES

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The tendency of tricalcium silicate to form solid solutions with other components is of great interest in the crystallochemistry of silicates and in the chemistry and technology of cements, refractories, etc.

Recent experimentation has shown that $3CaO \cdot SiO_2$ is capable of dissolving a certain amount of the oxides of chromium [1, 2], cobalt and nickel [3], iron, manganese, phosphorus [4], and also titanium. The problem of the solution of magnesium oxide and aluminum oxide (or calcium aluminates) in tricalcium silicate is a very significant one in the chemistry of cement. The composition of this solid solution, which has been given the name alite, is assumed to be $54\,CaO \cdot 16SiO_2 \cdot Al_2O_3 \cdot MgO$ [5]. Until recently, there has been some doubt as to the possibility of the formation of solid solutions between $3CaO \cdot SiO_2$ and $3SrO \cdot SiO_2$ [6]. The synthesis of tricalcium silicate itself was only accomplished in 1952 [6]; the first investigator to study the system $SrO-SiO_2$, Eskola, observed only two strontium compounds, the meta- and the orthosilicate [7].

According to reference [6], tricalcium and tristrontium silicates are not alike in either physical or chemical properties and have no tendency toward the formation of solid solutions. Nevertheless, further work has shown that these minerals are substantially similar. Thus, Massazza [8] was able to establish that strontium silicate exists in several polymorphic modifications. According to the data of reference [4], the phenomenon of polymorphism is a characteristic of calcium silicate also. Moreover, $3SrO \cdot SiO_2$, like $3CaO \cdot SiO_2$, is stable over a limited temperature region in comparable systems.

Further, one of the common properties, which is most important in cement chemistry, is the ability to harden when treated with water. In the opinion of Braniski [9], this quality is possessed by one of the varieties of $3SrO \cdot SiO_2$.

Finally, Carlson and Wells [10] were able to synthesize a strontium hydrosilicate, $3SrO \cdot SiO_2 \cdot 2H_2O$, similar in composition to the calcium hydrosilicate $3CaO \cdot SiO_2 \cdot 1.5H_2O$, which is formed during hydrothermal treatment of $3CaO \cdot SiO_2$.

The close similarity of the elements Ca and Sr, the similar ionic radii (Ca^{+2} 1.04 A, Sr^{+2} 1.20 A), and the analogy in the properties of the corresponding silicates considered above suggest that the silicates will form solid solutions. However, the very significant similarity in the optical indices of these minerals and the absence of color considerably hinders investigation. An even greater barrier is the limited region of stability of both compounds.

We have attempted to investigate the formation of solid solutions between these minerals and the limits of solubility of $3SrO \cdot SiO_2$ in calcium silicate.

Samples having the following compositions were synthesized: pure $3CaO \cdot SiO_2$, 95 wt.% $3CaO \cdot SiO_2$ + 5 wt.% $3SrO \cdot SiO_2$, 92.5 wt.% $3CaO \cdot SiO_2$ + 7.5 wt.% $3SrO \cdot SiO_2$, 90.0 wt.% $3CaO \cdot SiO_2$ + 10 wt.% $3SrO \cdot SiO_2$.

Natural calcite, rock crystal, and strontium carbonate were used as starting materials. The finely powdered, carefully mixed charge was tabletted and calcined for 100 hr at 1400° and then for 12-15 hr at 1550-1600° in a platinum crucible in furnaces with platinum and platinum–rhodium heaters. After each 10-15 hr heating period, the tablets were ground, tabletted again, and again calcined. The calcined samples were rapidly cooled by quenching in air.

Chemical analysis by the alcohol–glycerate method showed that after calcination under the regime indicated above, the samples containing 5 and 7.5% $3SrO \cdot SiO_2$ contained no free calcium oxide. Samples containing 10%

strontium silicate could not be prepared without free CaO, even by 40-50 hr exposure at 1550-1600°. Calcination of the samples at 1700-1800° in a microfurnace with a tungsten heater also did not lead to the desired results.

The optical analysis of the crystals was carried out under sodium light at constant temperature (22°). The results showed that samples containing 5 and 7.5% $3SrO \cdot SiO_2$ consisted of weakly birefringent grains of tricalcium silicate having indices of refraction somewhat higher than those of the pure material, specifically: Pure $3CaO \cdot SiO_2$ 1.717-1.720; with 7.5% $3SrO \cdot SiO_2$, 1.720-1.724.

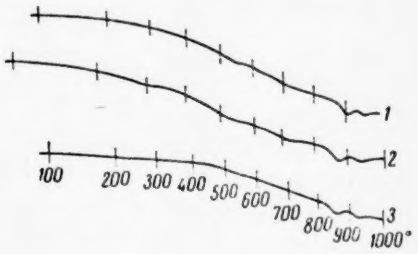

Fig. 1. Differential thermal analysis curves.

The difference in the indices of refraction of pure $3CaO \cdot SiO_2$ and the solid solution were so insignificant that it was necessary to confirm the chemical and optical data by differential thermal analysis and by x-ray analysis.

Figure 1, presents thermal analysis curves taken with a microthermal analysis apparatus with samples of pure $3CaO \cdot SiO_2$ (curve 1), 5% (curve 2), and 7.5% (curve 3) $3SrO \cdot SiO_2$. The difference between the polymorphic transformation temperature of tricalcium silicate with added $3SrO \cdot SiO_2$ and that of the pure mineral can be explained by the formation of a solid solution. The comparative values of the temperatures of the endothermic reactions are as follows: For pure $3CaO \cdot SiO_2$, the first transformation took place at approximately 900° and the second at 950°; for the solid solution containing 7.5% $3SrO \cdot SiO_2$, these temperatures were 850 and 920° respectively. The results of the thermal analysis of the pure $3CaO \cdot SiO_2$ are in agreement with the data of reference [11] with the only exception that the transformation temperatures were somewhat lower under our conditions. The existence of the endothermic reactions is probably due to polymorphic transformations of tricalcium silicate [4, 11]:

$$\text{Pure } 3CaO \cdot SiO_2 \text{ triclinic} \overset{900°}{\rightleftharpoons} \text{monoclinic} \overset{950°}{\rightleftharpoons} \text{trigonal.}$$

The addition of strontium ions either does not change the lattice, or it distorts the lattice so little that the high-temperature transformations of the solid solution are of apparently of the same nature as those of the pure mineral; specifically, the solid solution also has two polymorphic transformations.

X-ray analysis of the samples was carried out by an asymmetric method [12]. The photographs were taken with a precision cylindrical camera CuKα-radiation was used. The effect of luminescence was reduced through the use of aluminum foil. In order to obtain the sharpest possible interference lines, the samples were prepared by depositing the powdered sample on glass fibers having a thickness of 0.04-0.06 mm. The exposures were made at 18-19°. Measurement of the distances between the interference lines was accomplished by means of an IZA-2 horizontal comparator which had an accuracy of ± 0.01 mm.

Fig. 2. X-ray pattern of the solid solution containing 7.5% $3SrO \cdot SiO_2$; photograph taken by the asymmetric method.

Since it was not possible to obtain sharp lines at large values of θ, the effective diameter of the film was calculated from a pattern for metallic copper taken on this part of the x-ray photograph.

In Fig. 2 are shown x-ray photographs of the solid solution containing 7.5% $3SrO \cdot SiO_2$; the photograph was taken with a 55-hr exposure.

Although we were unable to obtain sharp lines at high values of θ, which would have yielded data of high accuracy, nevertheless, the accuracy proved to be quite satisfactory for present purposes. The arthmetic mean error in the average value of d was ± 0.001 and was approximately the same for all of the lines used.

Values of the interplanar distances* are presented below for pure $3CaO \cdot SiO_2$ and for its solid solution containing 7.5% $3SrO \cdot SiO_2$. Six of the sharpest and strongest interference lines at values of θ from 16.1 to 31.2° were selected for the calculations.

d_{av} of the pure $3CaO \cdot SiO_2$	2,7553	2,6028	2,1807	1,7605	1,5399	1,4855
d_{av} of the solid solution	2,7636	2,6120	2,1866	1,7663	1,5426	0,4893
d_{Δ}	0,0083	0,0092	0,0059	0,0058	0,0027	0,0038

Analysis of the x-ray data obviously indicates the presence of solid solutions in the system $3CaO \cdot SiO_2 - 3SrO \cdot SiO_2$ and confirms the results of the optical and differential thermal methods.

The limit of solubility of tristrontium silicate in tricalcium silicate is approximately 7.5 wt.%, according to our experimental data.

On the basis of existing concepts of isomorphism and of the rules governing the formation of solid solutions, it may be proposed that the present case is an example of substitution solid solutions or of solid solutions of the first type, and the ions replacing each other have the same valence. There has been comparatively little study of isovalent isomorphism of the pairs of ions $Ca^{2+} \rightleftharpoons Sr^{2+}$, but this case is of great interest in the crystallochemistry of silicates and the study of solid solutions.

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* Average values for four photographs taken with samples from two syntheses are cited.

TELOMERIZATION AND POLYMERIZATION OF ETHYLENE WITH SILANES IN THE PRESENCE OF TITANIUM TETRACHLORIDE

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In one of our earlier articles [1], we reported briefly on the titanium tetrachloride-catalyzed (initiated) telomerization of ethylene and propylene with methyldichlorosilane; the reaction takes place according to the equation:

$$CH_3SiCl_2H + nCH_2 = CHR \rightarrow CH_3SiCl_2(CH_2CHR)_nH.$$

The reaction was carried out at a pressure of about 200 atm and a temperature of 190-200°. Chlorostannic acid hexahydrate acts in a similar manner.

The reaction of ethylene with trichlorosilane, methyldichlorosilane, and triethylsilane in the presence of $TiCl_4$ was studied in the present work. The reaction was carried out in a steel autoclave under pressure and at elevated temperature. It was found that telomerization of ethylene proceeded smoothly and with good yields in the case of methyldichlorosilane and trichlorosilane.

Individual products having the structure $SiCl_3\,C_nH_{2n+1}$, where n = 2, 4, 6, and 8, were separated from the mixture of products resulting from the telomerization of ethylene with trichlorosilane in the presence of $TiCl_4$. The constants of these compounds and those of their methylation products were in agreement with those which we reported earlier [2]. The normal structure of the alkyl groups in these products was confirmed by a study of the i.r. spectra. A comparison of the yields of the individual telomeric homologs obtained by thermal telomerization with those of the products obtained in the presence of $TiCl_4$ is shown in Table 1.

TABLE 1

Experimental conditions	Conversion of $HSiCl_3$, %	Comparative yield, %				
		n = 2	n = 4	n = 6	n = 8	n > 8
Thermal reaction, 280°, 200 atm [2]	90	21.7	28	17.7	15	17.7
$TiCl_4$-Catalyzed reaction, 180°, 190 atm (Expt. B)	87	25	35.5	21	11.8	6.6
$TiCl_4$-Catalyzed reaction, 180°, 280 atm (Expt. A)	83	14.7	22.7	28.5	14.5	19.6

The reaction of methyldichlorosilane with ethylene, which was carried out in the presence of $TiCl_4$ at a temperature of 180-200° and a maximum pressure of 280 atm, resulted in the formation of a mixture of telomeric homologs having the structure $CH_3SiCl_2C_nH_{2n+1}$. The reaction was complicated by the formation of liquid hydrocarbons as a result of polymerization of the ethylene.

Individual methylalkyldichlorosilanes for which n = 2, 4, 6, and 8 (see Experimental, Expt. II) were separated from the reaction mixture.

Polymerization of the ethylene with the formation of polyethylene took place when triethylsilane was reacted with ethylene in the presence of $TiCl_4$ in an autoclave under pressure and at a temperature of 130°. No tolomeric products were detected. This difference in the courses of the reactions of these silanes with ethylene is apparently connected with the difference in their capabilities to act as reducing agents.

Fig. 1.

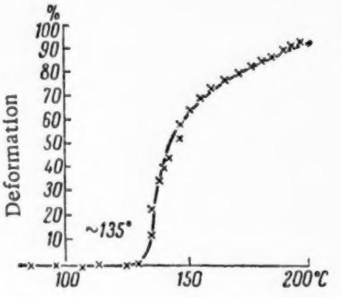

Fig. 2.

Triethylsilane, which has an electron-donor group bonded to the silicon, is a stronger reducing agent than trichlorosilane or methyldichlorosilane [3]. Therefore, it is possible that these silanes react with $TiCl_4$ to yield products of different degrees of reduction.

According to x-ray data* (see Fig. 1), the polyethylene obtained in this work was a crystalline material with a high degree of order in the crystalline areas.

A comparison of the x-ray pattern of the polyethylene synthesized in the present work with those of low-pressure polyethylene and of polymethylene prepared by decomposition of diazomethane** showed these three polymers to be identical.

According to the temperature-deformation curve (see Fig. 2), the polyethylene melts at 135°, which is in agreement with the melting point of low-temperature polyethylene. The molecular weight calculated from the viscosity of a solution of the polyethylene in tetralin at 135° was 26,670.

Thus, this method for the preparation of polyethylene – the polymerization of ethylene in the presence of triethylsilane and titanium tetrachloride – yields a product which is practically indistinguishable from the low-pressure polyethylene obtained by Ziegler. In a recently published work, Nitzsche [4] also noted that the interaction of ethylene with methylpolysiloxane (obtained by hydrolysis of methyldichlorosilane) in the presence of titanium tetrachloride also produces polyethylene.

EXPERIMENTAL

I. Telomerization of ethylene with trichlorosilane. A. To a half-liter stainless steel autoclave was charged 80 g of $HSiCl_3$ and 1 ml of $TiCl_4$; air was purged from the autoclave with nitrogen, and ethylene was introduced to a pressure of 55 atm. The autoclave was heated to 200°. The maximum pressure was 280 atm. The reaction was carried out at this temperature for 3 hr, during which time the pressure dropped to 160 atm. The experiment was repeated three times, and the four reaction products were combined and fractionally distilled.

A total of 320 g of $HSiCl_3$ was charged. There was obtained 394 g of reaction products. Fractional distillation yielded the following fractions:

Fraction No.	1	2	3	4	5	6	7	8	Residue
Temperature, °C	30–40	95–100	101–145	145–150	60–87 (30mm)	87–89 (30mm)	70–96 (10mm)	102 (10mm)	
Weight, g	36	48	2	71	4	93	2	47	64

A second distillation of fractions 2, 4, 6, and 8 yielded the corresponding individual alkyltrichlorosilanes. A comparison of the constants of these compounds with those of these same substances which we previously obtained by thermal telomerization is shown in Table 2.

These alkyltrichlorosilanes were methylated with methylmagnesium iodide. The constants of the resulting compounds are compared with the literature values [5] in Table 3.

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* The x-ray pattern and the temperature-deformation curve were obtained in the laboratories of x-ray structural analysis and polymer physics of the Institute of Heteroorganic Compounds.

** The x-ray patterns of these polymers were kindly loaned to us by V. A. Sergeev so that the above comparison could be made.

B. The experiment was carried out in the same manner as Expt. A, but the maximum pressure was 190 atm and dropped to 100 atm during the course of the reaction. From 80 g of $HSiCl_3$ was obtained 103 g of reaction products. Distillation yielded the following fractions:

Fraction No.	1	2	3	4	5	6	7	Residue
Temperature, °C	30--90	98--100	100--145	145	56—79(30 mm)	80(30 mm)	87(7 mm)	
Weight, g	12	19	3	26	6	16	9	5

II. Reaction of ethylene with methyldichlorosilane. The experiment was carried out in the manner of Expt. IA. A total of 60 g of CH_3SiCl_2H and 1 ml of $TiCl_4$ was charged to the autoclave. The maximum pressure reached 270-280 atm at a temperature of 190-200°, and it dropped to 150 atm during the course of the reaction. There was obtained 94 g of reaction products. The experiment was repeated three times, and the combined reaction products were distilled in a column. The individual methylalkyldichlorosilanes were obtained by distillation of 259 g of reaction mixture. The yields and constants of these compounds are given in Table 4; the constants of these same substances previously obtained by us by thermal telomerization are also shown for comparison.

TABLE 2

Compound	B. p., °C		n_D^{20}		d_4^{20}		MR	
	found	lit.	found	lit.	found	lit.	found.	calc.
$C_2H_5SiCl_3$	97	97—100	1,4248	—	1,2264	—	34,08	33,41
$C_4H_9SiCl_3$	146	146—151	1,4358	1,4352	1,1585	1,1577	42,92	42,71
$C_6H_{13}SiCl_3$	87 (30 mm)	87—89 (30 mm)	1,4435	1,4440	1,1092	1,1094	52,53	52,12
$C_8H_{17}SiCl_3$	102 (10 mm)	97 (10 mm)	1,4490	1,4490	1,0746	1,0744	61,81	61,41

TABLE 3

Compound	B, p., °C		n_D^{20}		d_4^{20}		MR	
	found	lit.	found	lit.	found	lit.	found	calc.
$C_2H_5Si(CH_3)_3$	62	62	1,3820	1,3828	0,6838	3,6849	34,78	34,83
$C_4H_9Si(CH_3)_3$	113	115	1,4035	1,4030 (at 25°)	0,7167	0,7181	44,42	44,12
$C_6H_{13}Si(CH_3)_3$	161—163	163	1,4162	1,4154	0,7418	0,7422	53,57	53,41
$C_8H_{17}Si(CH_3)_3$	82 (10 mm)	82,3 (10 mm)	1,4235	1,4242	0,7571	0,7581	62,76	62,70

TABLE 4

Compound	Yield, %	B. p., °C		n_D^{20}		d_4^{20}		MR	
		found	lit.	found	lit.	found	lit.	found	calc.
$C_2H_5SiCl_2CH_3$	18	100.5	100	1.4190	1,4240	1,0644	1,0655	33,94	33,87
$C_4H_9SiCl_2CH_3$	18	149	147—148	1,4320	1,4312	1,0212	1,0190	43,46	43,26
$C_6H_{13}SiCl_2CH_3$	25	90 (31 mm)	91 (32 mm)	1,4390	1,4390	0,9892	0,9931	52,95	52,59
$C_8H_{17}SiCl_2CH_3$	13	90 (6 mm)	94 (6 mm)	1,4450	1,4440	0,9684	0,9761	62,32	61,88

In addition, intermediate fractions boiling at 70-90° at 31 mm and 60-89° at 6 mm were obtained; these contained hydrocarbon impurities (increased carbon and hydrogen contents and decreased densities).

III. Reaction of triethylsilane with ethylene (preparation of polyethylene). To the autoclave was charged 40 g of $(C_2H_5)_3SiH$ and 2.5 ml of $TiCl_4$. Air was purged from the autoclave with nitrogen, and ethylene was introduced to a pressure of 50 atm. The reaction was carried out at 130°. The maximum pressure was 95 atm. The pressure dropped to atmospheric when the autoclave was heated for 2 hr. The reaction product, a dirty gray solid mass which turned white in air, was removed from the autoclave and purified by recrystallization from toluene.

Found %: C 84.98, 85.04; H 14.14, 14.15. $(CH_2)x$. Calculated %: C 85.63; H 14.37.

Determination of the molecular weight was carried out with a suspended-level Ostwald viscosimeter at 135° in tetralin at a concentration of 0.1 g/100 ml. Since η_{sp} at C = 0.1 g/100 ml ≈ [η], the formula given in reference [6] was used to calculate the molecular weight:

$$[\eta] = 2{,}4 \cdot 10^{-4} \cdot M_w^{0{,}78},$$

where [η] is the intrinsic viscosity and M_w is the average molecular weight. The molecular weight was found to be 26,670.

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WAYS OF SYNTHESIZING CYCLIC SYSTEMS OF "BA" TETRACYCLINES

SYNTHESIS OF ESTERS OF SUBSTITUTED 2-KETOCYCLOHEXYLACETIC ACIDS

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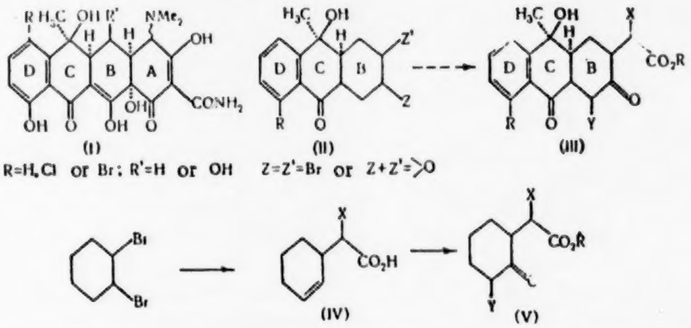
In connection with the problem of total synthesis of tetracyclines (I) we studied, on model compounds, the possible conversion of hydroanthracenic dibromides and epoxides (II), described before [1], to the tricyclic compounds of type (III); the latter have such X and Y substituents that they could eventually be converted to the dimethylamino and the ketonic carbonyl group, respectively. With this goal we prepared the first representative of type (V) from 1,2-dibromocyclohexane via an unsaturated acid (IV, X = AcNH), namely 3-bromo-2-ketocyclohexylaceturate (V, X = AcNH, Y = Br) [2]. While developing these studies, we presently synthesized a series of type (V) compounds, specifically ketonic esters (XIIIa) – (XIIIc) and (XVIIb), with which this paper is concerned.

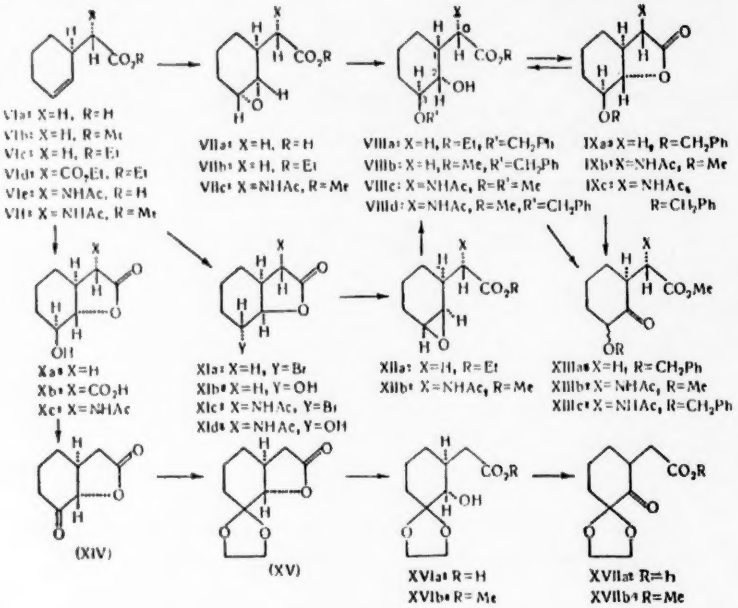


We prepared 2,3-α-epoxycyclohexylacetate (VIIb) in 85% yield by epoxidation of the ethyl ester of 2-cyclohexenylacetic acid (VIc) by means of $PhCO_3H$ in chloroform solution. The stereoisomeric β-epoxyester (XIIa) was formed in almost quantitative yield by the action of 0.5 N ethanolic KOH solution on the bromolactone (XIa), which in turn was obtained by bromination of 2-cyclohexenylacetic acid (VIa) in a soda solution [2, 3]. Both isomeric epoxy esters – (VIIb) and (XIIa) – gave one and the same hydroxybenzyloxy ester (VIIIa) by the action of benzyl alcohol in the presence of BF_3 at 20°. The ester (VIIIa) really could not be isolated as an individual compound, since it partially lactonized when distilled. On the other hand, when this hydroxybenzyloxy ester was saponified, it gave the pure benzylhydroxylactone (IXa) in 70% yield with ease. This was converted to the hydroxybenzylhydroxy ester (VIIIb) (76% yield) by the action of methanolic KOH followed by $AgNO_3$ and MeI.

Analogously, we converted the epoxy esters (VIIc) and (XIIb), synthesized by us earlier from the unsaturated ester (VIf) and the bromolactone (XIc) [2], to hydroxybenzylhydroxy ester (VIIId) by the action of $PhCH_2OH$ in the presence of BF_3 or H_2SO_4; the product was purified via lactone (IXc). Methanolysis of epoxy esters (VIIc) and (XIIb) gave the hydroxymethoxy ester (VIIIc) in 94 and 80% yields.

Oxidation of hydroxyalkoxy esters (VIII) to alkoxy ketonic esters (XIII) presented certain difficulties caused by the considerably shielded position of the hydroxyl group in the starting compounds, and the pronounced tendency of the acyloin esters formed to be hydrolyzed by acids and bases. For this reason the reaction was first studied with trans-2-benzylhydroxy cyclohexanol as an example; it was shown, that the oxidation conditions recommended by Mousseron [4] – H_2CrO_4 in H_2SOR solution – give unsatisfactory results (about 15% yield), while the use of CrO_3 in

pyridine (20°, 24 hr) as the oxidizing agent gave 50% of 2-benzylhydroxycyclohexanone isolated in the form of the semicarbazone.* This kind of oxidation of hydroxy esters (VIIIb) – (VIIId) gave the corresponding ketonic esters (XIIIa)–(XIIIc) in 60–80% yield.



The ketal lactone (XV) necessary for the preparation of the ketal ketonic ester (XVIIb was synthesized from 2-cyclohexenylmalonic ester (VId) vis (Xb), (Xa), or (XIV) according to the scheme described earlier [6]; a method variation consisting of decarboxylation of the intermediate carboxylactone (Xb) in boiling pyridine enabled us to obtain the trans-hydroxylactone (Xa) in a crystalline state for the first time. Direct oxidation of the ketal lactone (XV) with $Mg(OBr)_2$ according to McRae [7] gave the ketonic acid (XVIIa); the yield of the latter, however, did not exceed 15%, in contrast to data by Rosenmund [6]. For this reason the lactone (XV) was first saponified to the corresponding hydroxyacid (XVIa), which then was treated with CH_2N_2 or by methylation of its Ag salt with CH_3I to give the methyl ester (XVIb). Oxidation of the latter with ditertiary butyl chromate** yielded 55% of the ketal ketonic ester (XVIIb), which could also be obtained by methylation of acid (XVIIa) by means of CH_2N_2.

The structure of the compounds described here (their constants and analytical data are given in the table) was established as follows. Alcoholysis of α-epoxy ester (VIIc) by methanol or benzyl alcohol in the presence of the corresponding alcoholates gave the same hydroxyalkoxy esters (VIIIc) and (VIIId), which are formed by the interaction of epoxy ester (VIIc) with MeOH or $PhCH_2OH$ under the effect of BF_3 or H_2SO_4. While it is known that alcoholysis of epoxides which is catalyzed by alkalies represents an S_{N_2} reaction, the acid alcoholysis proceeds by the carbonium mechanism [9]. It thus seemed probable, that hydroxyalkoxy esters (VIII) are obtained from α-epoxides (VII) through an attack of the alkoxyl anion in the 3β-position (least shielding) while preserving configuration C_2, while the formation of those same compounds from β-epoxides (XII) is connected with inversion of the asymmetric center 2. The correctness of this assumption was then strictly proved by hydrogenolysis of benzylhydroxy lactones (IXa) and (IXc) to trans-hydroxy lactones (Xa) and (Xc); the latter had been synthesized earlier [2, 6] together with the cis-isomers (XIb) and (XId) by hydroxylation of the unsaturated acids (VIa) and (VIe) by means of HCO_3H. In this manner the hydroxy alkoxy esters (VIII) have the cis-configuration in the substituents on asymmetric centers 1 and 3, and these substituents obviously are in the thermodynamically most stable 1,3-cis-diequatorial configuration. Evidently this same configuration should be preserved in the products, i.e., the ketonic esters, and consequently their most likely steric structure is (XIII).

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* 2-Benzylhydroxycyclohexanone was also synthesized by us in 45% yield by the etherification of 2-hydroxycyclohexanone (adipoin) with benzyl alcohol in the presence of HCl (see [5]).

** Hydroxy ketals of this type e.g., ethylene ketals of adipoin, can be satisfactorily oxidized with the complex $CrO_3 \cdot 2Py$, despite literature data [8]. The best results, however, are obtained with the use of tert-Bu_2CrO_4.

The structure and configuration of the bromolactone (XIa) was proved by reduction-dehalogenation of the compound in the presence of gauge PdO or Ni; the product was the lactone of cis-2-hydroxycyclohexylacetic acid known before [10]; The cis-linkage of the lactone and cyclohexane rings in compound (XIa) naturally is explained by the β-configuration of the oxide ring in the epoxy ester (XIIa). As to the structures of the other compounds, no special explanation is necessary.

Compound	M. p. (decomp.), b. p., solvent for crystallization	Found, %			Calculated, %		
		C	H	N	C	H	N
VIb	80—81°/10 mm	70,31	9,29		70,10	9,15	
VIc	85—86°/10 mm	71,22	9,72		71,39	9,59	
VIIa	s-Benzylthiuronic salt 153—154° (EtOH)	59,22	6,91		59,60	6,88	
VIIb	92—93°/1 mm	65,18	8,90		65,19	8,75	
VIIIb	165—167°/1 mm	69,37	7,81		69,04	7,97	
VIIIc	113—114° (AcOEt—Et_2O)	55,59	8,26	5,52	55,58	8,16	5,40
VIIId	41—42° (AcOEt—Et_2O)	64,28	7,47	4,23	64,46	7,51	4,18
IXa	173—175°/1 mm	72,92	7,43		73,14	7,37	
IXb	147—148° (AcOEt—MeOH)	57,92	7,55	6,01	58,13	7,54	6,16
IXc	68—69° (AcOEt—Et_2O)	67,29	7,06	4,66	67,31	6,98	4,62
Xa	39—40° (Et_2O)	61,23	7,74		61,52	7,75	
	3,5-Dinitrobenzoate 112—113° (EtOH)	51,48	4,15		51,43	4,03	
Xc	167—168° (AcOEt)	56,32	7,14	6,66	56,32	7,09	6,57
	3,5-Dinitrobenzoate 230—231° (EtOH)	49,84	4,32	10,15	50,12	4,21	10,32
XIa	58—59° (Et_2O—hexane)	43,85	5,06		44,06	5,15	
XIIa	87—88°/1 mm	64,93	8,75		65,19	8,75	
XIIIa	148—150°/0,5 mm	69,46	7,35		69,54	7,30	
	Semicarbazone 139—140° (MeOH)	60,98	6,97	12,95	61,24	6,95	12,61
XIIIb	71—73° (AcOEt—Et_2O)	55,88	7,41	5,71	56,02	7,44	5,44
XIIIc	59—60° (AcOEt)	65,19	7,19	4,25	64,85	6,95	4,20
XVIb	135—137°/1 mm	57,69	7,59		57,38	7,88	
XVIIb	63—64° (MeOH)	57,56	7,04		57,88	7,07	

In this manner we have synthesized a number of new ketonic esters of type (I), which can be used to prepare bicyclic systems of "BA" tetracyclines by utilizing various addition reactions at the ketonic group (acetylation, cyanohydrin synthesis, Norman reaction, etc.).

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2-β-HYDROXYETHYL-2-PHENYLINDANDIONE-1,3

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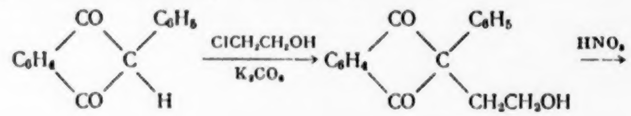
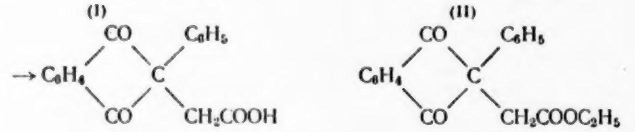
Some 2-substituted indandiones-1,3 are good blood anticoagulants. For instance 2-phenylindandione-1,3 (I) is already being used in medical practice under the name "Phenilin," and is considered a better anticoagulant than dicoumarin which up to now has been used in the USSR [1-3]. Other active blood anticoagulants are: 2-Anisylindandione-1,3 [4], 2-naphthylindandione-1,3 [5, 6], and specially 2-diphenylacetylindandione-1,3 ("Diphenacin") [7, 8]. It is believed [9] that the anticoagulation action of compounds in the hydroxycoumarin and indandione-1,3 series is connected with their ability to form enols. However, one of us, in collaboration with M. N. Koptelova [10] was able to show that anticoagulation activity is not essentially impaired by substitution of the active hydrogen in phenylindandione with chlorine, bromine, a nitro or hydroxymethyl group. From among these derivatives, 2-hydroxymethyl-2-phenylindandione-1,3 under the name "Omephin" was proposed for clinical use [11]. This gave rise to an interest in preparing the next homolog – 2-β-hydroxyethyl-2-phenylindandione-1,3 (II).

2-Phenylindandione-1,3 usually is alkylated in the 2-position by the action of a halide on its salt [12, 13]. We hydroxyethylated 2-phenylindandione-1,3 without first preparing its salt, simply by prolonged heating of 2-phenylindandione-1,3 with an excess of ethylene chlorohydrin at 140° in the presence of K_2CO_3. Replacement of the excess ethylene chlorohydrin by an alcohol did not give satisfactory results.



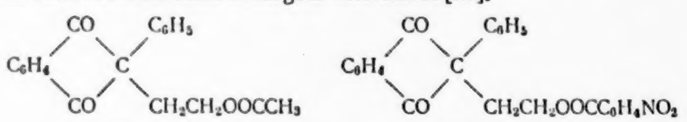
(I) (II)



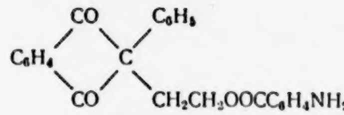
(III) IV

The 2-β-hydroxyethyl-2-phenylindandione-1,3 (II) thus obtained is a white, crystalline substance melting at 154°. Its oxidation with HNO_3 gave the corresponding acid: 2-carboxymethyl-2-phenylindandione-1,3, or 2-phenylindandionyl-(2)-acetic acid (III). The ethyl ester (IV) of the acid was prepared via the acid chloride. The ester and the acid itself, although prepared differently, have been described in the literature.

When 2-β-hydroxyethyl-2-phenylindandione-1,3 was boiled with acetic anhydride; the corresponding acetate (V) melting at 77° was formed. Analogously, p-nitrobenzoate (VI) was obtained with p-nitrobenzoyl chloride. Its reduction gave p-aminobenzoate (VII). This is an analog of anesthesine (benzocaine), in which the β-hydrogen of the ethyl group is substituted by the phenylindandionyl radical. The substance is rather unstable, and mineral acids turn it brown, probably as a result of facile polycondensation between the aromatic amino group and the carbonyl group; this has also been observed with other analogous derivatives [14].



(V) (VI)



VII

According to preliminary results, 2-β-hydroxyethyl-2-phenylindandione-1,3, unlike 2-β-hydroxymethyl-2-phenylindandione-1,3, has no anticoagulation properties.

EXPERIMENTAL

2-β-Hydroxyethyl-2-phenylindandione-1,3. Fifty g (0.225 mole) 2-phenylindandione-1,3,47 g (0.350 mole) K_2CO_3, and 62 ml (0.923 mole) ethylene chlorohydrin was heated on an oil bath at 140° (bath temp). The resulting red solution was poured into water, the precipitate which formed separated, washed with a soda solution and crystallized from 120 ml alcohol. This gave 42 g (70%) of 2-β-hydroxyethyl-2-phenylindandione-1,3. White crystals, m. p. 154°. The compound is readily soluble in benzene, alcohol, ethyl acetate, dichloroethane, chloroform, and ether. With concentrated sulfuric acid it gives a violet solution.

Found %: C 77.00; H 5.30. $C_{17}H_{14}O_3$. Calculated %: C 76.68; H 5.26.

When 2-β-hydroxyethyl-2-phenylindandione was removed from the red aqueous solution and the filtrate was acidified with HCl, 2.5 g of unreacted 2-phenylindandione-1,3 (m. p. 146°) was obtained, so that the overall yield of 2-β-hydroxyethyl-2-phenylindandione-1,3 was 73.5% of the theoretical, based on phenylindandione-1,3 entering the reaction.

2-Carboxymethyl-2-phenylindandione-1,3 (III). 5.32 g of 2-β-hydroxyethyl-2-phenylindandione-1,3 was digested with 50 ml HNO_3 (d = 1.35) until no more nitrogen oxides evolved, and then diluted with water. The precipitate was recrystallized several times from benzene. This gave 1.68 g (30%) of 2-carboxymethyl-2-phenylindandione-1,3, or 2-phenylindandionyl-(2)-acetic acid. The white crystals melted at 214-215°, which was in accord with the literature [13]. The product easily dissolved in alcohol, dioxane, glacial acetic acid, and in sodium bicarbonate.

Found %: C 72.91; H 4.48. $C_{17}H_{12}O_4$. Calculated %: C 72.85; H 4.32.

The ammonium salt. 2.8 g of acid III was dissolved in 10 ml ammonia, evaporated to dryness, and the residue crystallized from alcohol to which ether was added. This gave 2.1 g (75%) of the ammonium salt. The white crystals melted at 175° (decomp.). The salt readily dissolved in water; acidification of the solution again yielded acid III.

Found %: N 4.57. $C_{17}H_{15}O_4N$. Calculated %: N 4.71.

The ethyl ester. 2.8 g of acid III and 11.9 g thionyl chloride was digested for 30 min, and after cooling poured into 10 ml alcohol. The solution thus obtained was diluted with 50 ml water, and the resulting precipitate recrystallized from alcohol. This gave 2.34 g (76%) of the ethyl ester of acid III. Melting point 105-106°, which corresponds with literature data (104°) [12]. The compound readily dissolved in alcohol, benzene, and dioxane.

The acetate of 2-β-hydroxyethyl-2-phenylindandione-1,3 (V). 2.66 g of 2-β-hydroxyethyl-2-phenylindandione-1,3 was digested with 20 ml acetic anhydride for 30 min. The cooled solution was poured into water. After decomposition of the acetic anhydride the precipitate was twice recrystallized from alcohol. This gave 2.93 g (77%) of the acetate of 2-β-hydroxyethyl-2-phenylindandione-1,3. The white crystals melted at 77°. The compound readily dissolved in benzene, methanol, ethanol, and glacial acetic acid.

Found %: C 74.47; H 5.09. $C_{19}H_{16}O_4$. Calculated %: C 74.01; H 5.23.

p-Nitrobenzoate of 2-β-hydroxyethyl-2-phenylindandione-1,3 (VI). 2.66 g (0.01 mole) of 2-β-hydroxyethyl-2-phenylindandione-1,3 and 2.04 g (0.011 mole) of p-nitrobenzoyl chloride in 20 ml dry benzene was digested for 5 hr The resulting crystals were recrystallized from a mixture of alcohol and dioxane. This gave 2.49 g (50%) of p-nitrobenzoate of 2-β-hydroxyethyl-2-phenylindandione-1,3. The white crystals melted at 156°. The compound readily dissolved in glacial acetic acid, dioxane, and dissolved poorly in methanol, ethanol, and benzene.

Found %: N 3.58. $C_{24}H_{17}O_6N$. Calculated %: N 3.37.

p-Aminobenzoate of 2-β-hydroxyethyl-2-phenylindandione-1,3 (VII). To a solution of 4.154 g of the p-nitrobenzoate of 2-β-hydroxyethyl-2-phenylindandione-1,3 in 40 ml glacial acetic acid was added zinc dust, and the mixture boiled with more zinc dust added now and then up to a total of 6.4 g. At first the solution was yellowish-brown, then it turned colorless. After completed reaction the filtrate was diluted with water, the white precipitate separated and washed thoroughly with water. This gave 3.81 g (98%) of the p-aminobenzoate of 2-β-hydroxyethyl-2-phenylindandione-1,3, m. p. 97-100° (decomp.). The compound readily dissolved in methanol, ethanol, and did not dissolve in dichloroethane and CCl_4. Elevated temperatures and also mineral acid change and darkened the compound easily. We did not succeed in recrystallizing it.

Found %: N 3.73. $C_{24}H_{19}O_4N$. Calculated %: N 3.64.

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OPTICAL STUDIES OF THE STRUCTURE OF 2-METHYL-1-HYDROXYCYCLOHEXYLETHYLENE OXIDES

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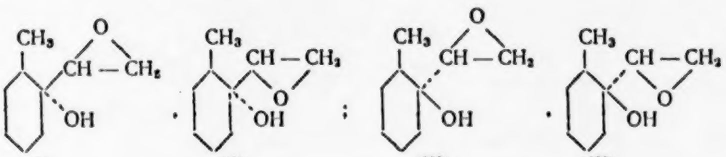
One of the authors [1] oxidized cis-2-methyl-1-vinylcyclohexanol with peracetic acid in chloroform and obtained two glycidic alcohols with the cis-configuration; when the trans-2-methyl-1-vinylcyclohexanol was oxidized, two glycidic alcohols with the trans-configuration were the products (the reactions proceed with preservation of the configuration at the asymmetric center). It was assumed that in each pair the alcohols differ from each other in steric position of the oxide ring, and are diastereoisomers, i.e., that the following four glycidic alcohols were formed: (I) cis-erythro-(2-methyl-1-hydroxycyclohexyl)ethylene oxide, (II) cis-threo-(2-methyl-1-hydroxycyclohexyl)ethylene oxide, (III) trans-erythro-(2-methyl-1-hydroxycyclohexyl)ethylene oxide, and (IV) trans-threo-(2-methyl-1-hydroxycyclohexyl)ethylene oxide:



(I) (II) (III) (IV)

All four alcohols have very different melting points: one of the cis-series melts at 43-43.5°, the other is liquid (b. p. 89-90° at 7 mm); one alcohol of the trans-series melts at 75-75.5°, the other at 40.5-41°.*

A better understanding of the glycidic alcohol structures is possible from studies of combination light scattering spectra of those products. This showed, that in all four alcohols in the liquid state the hydroxyl group is part of the hydrogen bond with the oxide ring oxygen atom: The frequency of O—H is diffused to a band (see the table). For two trans-isomers the band is essentially different: The isomer with lower m. p. (40.5-41°) has a narrow band (about 45 cm^{-1}) but with a weakly intense diffusion towards the lower frequencies; the isomer with higher m. p. (75-75.5°) has a wider band (about 200 cm^{-1}) and relatively even intensity throughout the width. This indicates [3] an absolute predominance of an intramolecular hydrogen bond in the first of the two trans-isomers, and in the other an intermolecular hydrogen bond, i.e., that the first is compound (V), m. p. 40.5-41°, and the second one compound (III), m. p. 75-75.5°. Obviously it is this difference in types of hydrogen bonds which in this case is specifically expressed by the different melting points. If this also explains the greater difference in melting points of two cis-glycidic alcohols, then one of the alcohols with the higher melting point and also in that case with the intermolecular hydrogen bond is compound (I), m. p. 43-43.5°, while the other, liquid and with intramolecular hydrogen bonding, is compound (II). Optical data confirm the following: In the case of (II), O—H is sharply distinguished on the high frequency side of the band, and there also is a narrow intense band about 3520-3565 cm^{-1} somewhat separated from the rest of the band; this indicates a predominance of intramolecular hydrogen bonding in (II), in contrast to (I), where there is no sharp manifestation of a similar band due to the predominance of intermolecular hydrogen bonding. In contrast to the threo-isomer (IV), however, threo-isomer (II) has a rather intense band in the low frequency part (about 3390-3520 cm^{-1}). This indicates, that in the liquid state the O—H group of (II) is liberated from the intramolecular hydrogen bonding in a considerable portion of molecules, and that it enters the intermolecular bonding, i.e., that the threo-

* For nuclear magnetic resonance studies of these compounds see [2].

isomer partially is converted to the erythro-isomer or close to it from the position of the oxide ring. With (I) the transition of the erythro- to the threo-isomer is hardly detectable optically.

Vibration Frequencies of Hydroxyl, Oxide Ring, and Cyclohexane Ring (in cm^{-1})

Groups	Liquid state				20% solution in CCl_4			
	(I)	(II)	(III)	(IV)	(I)	(II)	(III)	(IV)
O–H	3390–3570; band	3520–3565; 3390–3520; bands	3390–3590; band	3520–3565; band	3541 (1*) 3565 (2*) 3612 (0) 3621 (1)	3525 (1*) 3552 (2*) 3612 (0) 3623 (0)	3542 (1*) 3563 (3*) 3613 (0) 3621 (0)	3527 (1*) 3550 (2*) 3613 (0) 3626 (0)
	1250 (2*) 1257 (9*) 1268 (2* db)	1252 (2* db) 1265 (9* db)	1252 (7 db) 1268 (1 db)	1252 (1 db) 1269 (6 db)	1249 (1*) 1255 (5*) 1269 (1 db)	1252 (1* db) 1264 (5* db)	1252 (5 db) 1268 (0 db)	1253 (1 db) 1269 (4 db)
	703 (8 db) 714 (2 db)	702 (8 db) 713 (3 db)	700 (1 db) 718 (7 db)	703 (1 db) 716 (8 db)	700 (4 db) 714 (1 db)	701 (4 db) 715 (2 db)	701 (1 db) 719 (4 db)	699 (1 db) 715 (4 db)

* With weak diffusion in the low frequency direction.

The basic stabilizing factor in the erythro-threo isomerism under question appear to be the two kinds of hydrogen bonds. The bond energy of those is not high (~ 3 kcal mole). For this reason the alcohols under investigation in their crystalline state show great differences between the erythro- and threo-isomers, but under our experimental conditions [liquid at ~30° for (II) and at ~85° for (III); supercooled liquid at ~30° for (I) and (IV); under the reaction conditions, exposure to light quanta of the blue and near ultraviolet regions] the stabilizing effect of the hydrogen bonds was impaired. Even under these conditions the approximate sequence is preserved, specifically, the four configurations of the alcohols under investigation as erythro- and threo-isomers remain preeminent.

In 20% solutions of the alcohols in CCl_4* the intramolecular hydrogen bonding as a rule is not disturbed [3]; this is confirmed optically by the observation that in the formerly described region the narrow band of the hydroxyl frequency of (II) and (IV) is preserved. Multiple complexes associated through intermolecular hydrogen bonds in the case of compounds (I) and (III) are disturbed, but under the conditions it is obvious that dimeric complexes are preserved (closer arrangement); monomers are also present. This is confirmed optically by the fading of the O–H band, the appearance of the narrow band in the ~3540-3565 cm^{-1} region, and weak doublets of O–H frequencies of the separate molecules: ~3612-3621 cm^{-1}. The aforesaid narrow bands also appear as doublets. In accord with our previous studies (see reference in [4]), the higher frequency of each of these doublets characterizes axial hydroxyl, and the lower frequency equatorial hydroxyl. In almost all isomers the higher frequencies in O–H doublets have greater intensity, only with (II) the intensities of both frequencies are approximately equal. All this shows, that each one of the four alcohols, under the experimental conditions, exists in two conformations, among which the more predominant conformation is (labeled according to the largest substituent – oxide ring or methyl group): for (I) – cis-ea, for (III) and (IV) trans-ee; for (II) both conformations are represented in about equal amounts (see the figure).

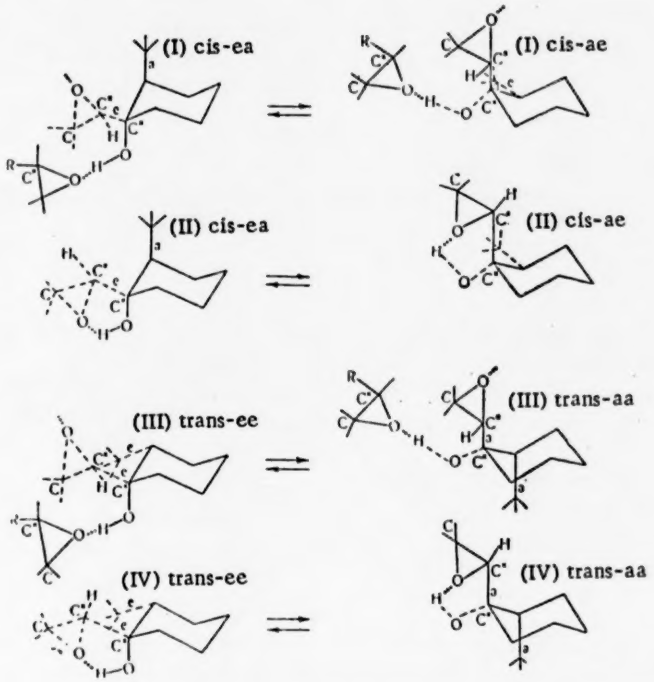
In the spectrum of ethylene oxide the oxide ring is characterized by the frequency of the pulsating vibrations of the three-membered ring, 1269 cm^{-1} [5]. A similar frequency (in the range 1264-1269 cm^{-1}) of the oxide ring also characterizes the spectra of threo-isomers (II) and (IV); in the spectra of erythro- isomers (I) and (III) this frequency is somewhat lower, in the range 1252-1257 cm^{-1} (see the table). Under our experimental conditions is seems that the erythro- and threo-isomers change from one to the other to some extent, as shown by the preservation of the less intense frequency ~1252 cm^{-1} in spectra of the threo- isomers and of ~1269 cm^{-1} in the spectra of the erythro-isomers.

The doublet character of the lines indicates the existence of alcohols in two different conformations. In spectrum (I) the doublet 1250, 1257 is rather clearly resolved.

In the spectra of alcohols under consideration (see the table) there is a double more intense frequency and another, also double, which is quite less intense, both in the region of frequencies of the pulsating vibrations of the ortho substituted cyclohexane ring (~700-720 cm^{-1}). In accord with our previous studies [6], compounds (I) and (II)

* Intensities of solution frequencies are not comparable with intensities of frequencies of liquid alcohols. The solutions were photographed at much greater exposure.

with intense lower frequencies of the pulsating ring vibrations (~699-703 cm^{-1}) have the cis-configuration, but compounds (III) and (IV) with intense higher frequencies of those vibrations (~713-719) have the trans-configuration. The weakening in the frequency intensity indicates the mixing in of one configuration with the other [specially in (II)]. The double character of the frequencies in question indicates that each alcohol, under our experimental conditions exists in two conformations, as noted in the figure.



Spectra of the combination light scattering were taken on a domestic spectrograph ISP-51 with a medium camera, and on a Hiller E612 spectrograph from the excited blue line 4358 A of a mercury lamp (for notation of frequency rates see [4]).

(I) cis-Erythro-(2-methyl-1-hydroxycyclohexyl)ethylene oxide. $\Delta\nu$ cm^{-1}: 181 (2*), 192 (3*), 199 (2*), 263 (1**), 276 (0**), 287 (3), 303 (1), 323 (2), 371 (2*), 387 (4*), 395 (4*), 408 (0), 452 (5), 485 (6), 509 (0), 530 (4), 539 (0), 551 (6 db), 566 (0), 586 (4 db), 703 (8 db), 714 (2 db), 787 (7), 812 (4*), 825 (4*),839 (4), 861 (6), 875 (4), 895 (3*), 904 (4*), 945 (5**), 956 (5**), 982 (6*),992 (2*), 1004 (7*), 1057 (3**), 1085 (5**), 1135 (6), 1144 (0), 1161 (6),1181 (3 db), 1223 (2 b), 1250 (2*), 1257 (9*), 1268 (2* db), 1275 (1*), 1304 (2), 1332 (1*), 1343 (4*), 1354 (4*), 1443 (8**), 1452 (8**), 1464 (3**), 1476 (1**), 2665 (3 b, band), 2853 (6*), 2863 (6*), 2899 (3*), 2912 (3*), 2930 (10*), 2941 (10*), 2954 (3*), 2999 (4**), 3014 (4**), 3390-3570 (5; band with a set of frequencies on it).

(II) cis-Threo-(2-methyl-1-hydroxycyclohexyl)ethylene oxide. $\Delta\nu$ cm^{-1}: 180 (2)*, 189 (3*), 206 (2*), 264 (1**), 270 (0**), 287 (3), 309 (1), 321 (1*), 331 (3*), 371 (1), 383 (4*), 394 (4*), 411 (0), 455 (5), 486 (6), 509 (1), 527 (2*), 539 (2*), 549 (6* db), 564 (0), 586 (5 db), 702 (8 db), 713 (3 db), 788 (8), 822 (5), 837 (6), 861 (6), 877 (4), 893 (4*), 904 (3*), 950 (5**), 961 (3**), 978 (6*), 992 (2*), 1005 (6* db), 1059 (3**), 1084 (5**), 1119 (1*), 1133 (6*), 1144 (0), 1159 (6), 1181 (3 db), 1232 (2), 1252 (2* db), 1265 (9* b, db), 1275 (2*), 1307 (2), 1332 (1*), 1342 (4*), 1353 (4*), 1443 (8**), 1451 (8**), 1465 (3**), 1479 (1**), 2663 (3 b, band), 2853 (6*), 2863 (6*), 2902 (3*), 2915 (3*), 2929 (10*), 2943 (10*), 2955 (3*), 2991 (4**), 3011 (4**), 3390-3520; 3520-2565 (5; bands adjoining one another).

(III) trans-Erythro-(2-methyl-1-hydroxycyclohexyl)ethylene oxide. $\Delta\nu$ cm^{-1}: 183 (2), 189 (0), 203 (2), 230 (0), 263 (2 db), 286 (1), 296 (3*), 306 (3*), 325 (0), 350 (3*), 358 (3*), 440 (6**), 448 (6**), 461 (3**), 485 (0), 569 (1), 582 (5), 597 (2), 609 (2*), 615 (0*), 634 (0), 680 (0), 700 (1 db), 718 (7 db), 777 (2*), 796 (5*), 833 (6),

865 (6*), 878 (2*), 892 (1*), 964 (4), 980 (1*), 993 (1*), 1004 (1*), 1051 (2**), 1066 (4**), 1078 (2**), 1108 (2), 1134 (4), 1157 (4), 1183 (6*), 1213 (6*), 1229 (1), 1252 (7 db), 1268 (1 db), 1274 (1), 1298 (0), 1311 (0), 1326 (0*), 1342 (2*), 1361 (1*), 1441 (6**), 1453 (5**), 1463 (3**), 1479 (2**), 2665 (3 b, band), 2849 (6*), 2868 (6*), 2904 (3*), 2921 (3*), 2928 (10*), 2941 (10*), 2952 (3*), 2991 (3**), 3009 (3**), 3390-3590 (5; band with a set of frequencies on it).

(IV) trans-Threo-(2-methyl-1-hydroxycyclohexyl)ethylene oxide. $\Delta\nu$ cm^{-1}: 182 (2), 191 (0), 203 (1), 229 (0), 266 (3 db), 286 (1), 296 (4*), 306 (4*), 320 (0), 349 (4*), 359 (4*), 440 (6**), 448 (6**), 463 (5), 487 (0), 566 (0), 579 (5), 593 (0), 607 (4*), 616 (4*), 634 (0), 681 (0), 703 (1 db), 716 (8 db), 794 (6), 835 (6), 861 (4), 885 (4*), 896 (2*), 957 (4), 981 (0*), 990 (5*), 998 (5*), 1056 (3**), 1068 (5 s**), 1081 (3**), 1120 (5*), 1136 (2*), 1154 (5*), 1187 (6), 1229 (4), 1252 (1 db), 1269 (6 db), 1275 (3), 1306 (0), 1330 (0*), 1344 (3*), 1357 (2*), 1436 (5**), 1449 (6**), 1465 (3**), 1478 (2**), 2663 (3 b, band), 2852 (6*), 2860 (6*), 2904 (4*), 2917 (3*), 2927 (10*), 2940 (10*), 2954 (3*), 2996 (4**), 3007 (4**), 3520-3565 (5; band slightly washed out in the lower frequency region).

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SOME RESULTS ON THE X-RAY SPECTROSCOPY OF FERROCENE AND DERIVATIVES

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Not long ago molecular orbitals and the distribution of electron charges in aromatic complexes were computed by E. M. Shusterovich and M. E. Dyatkina [1-3]. Interest was roused in verifying some of the theory conclusions by studying the fine structure of x-ray absorption spectra of a metal in these compounds. Such a study of x-ray spectroscopic data has in principle been made feasible by last year's development on the theory of x-ray spectra and a refinement of calculation methods for their fine structure [5-9]; see also [4].

Basic experimental data on x-ray absorption spectra of transition metals in many bis(cyclopentadienyl) compounds have been made available in [10-13]. In 1958 we also studied, in our laboratory,* the fine structure of K-absorption spectra of iron in $Fe(C_5H_5)_2$ and $Fe(C_5H_5)_2Cl$. These data served as a basis for further theoretical studies. X-ray K-absorption spectra of iron in potassium ferro- and ferricyanides, and also in $FeSO_4 \cdot 7H_2O$ and $Fe(NO_3)_3$ were prepared, for comparison under the same conditions. Table 1 gives the figures illustrating the relative positions of the principle maxima on x-ray absorption spectra of iron in the compounds under investigation. It can be seen that our measurements relating to the first four compounds are in good agreement with literature data [14]. Spectra were studied by means of a focus x-ray spectrograph for reflection and were photographically recorded in light falling perpendicularly to the film. Reflecting crystal – quartz, facet $(13\bar{4}0)$. Comparison line – Co $K_{\alpha 1,2}$. Exposure – three to 6 hr. Cycle – 15 kv and 50 ma. Effective caliber of the absorption apparatus – 5 mg/cm^2.

TABLE 1

Compound	$FeSO_4 \cdot 7H_2O$	$K_4[Fe(CN)_6]$	$K_3[Fe(CN)_6]$	$Fe(NO_3)_3$	$Fe(C_5H_5)_2$	$Fe(C_5H_5)_2Cl$
Energy, ev	0	1,9	3,8	6,8	6,1	6,1

Figure 1 compares x-ray K-absorption spectra of iron in $Fe(C_5H_5)_2$ and $Fe(C_5H_5)_2Cl$, after their adjustment to apparatus deviations. Along the abscissa are the energies of x-ray quanta, read from an arbitrary zero; along the ordinate are the magnitudes proportionate to the absorption coefficient. It can be seen that the K-absorption edges of iron in both compounds are mostly analogous, and the spectra differ only in the course of the absorption coefficient variations in the edge of greatest wavelength.

When computing the experimental absorption edges for iron in the complexes under question, we started with the assumption – several times proved in [6, 15, 16] – that there is a similarity with the hydrogen system, where in the gaseous molecules or crystalline complexes with approximately central symmetry of the field an electron liberated from the K-film moves beyond the limits of the filled films of the absorbing atoms. The following relationships serve to compute, within the approximation, the system of selective absorption lines and the continuous edge (at the same time forming the fine structure of the principle K-absorption edge of the element in the compound):

$$\varepsilon_n = \varepsilon_\infty - \frac{\eta^2}{n^2}\,\mathrm{Ry}; \tag{1}$$

* Presented at the All-Union Conference on X-ray Spectroscopy in Rostov-on-the Don, June 30, 1959.

$$\frac{\tau_n}{\tau_\infty} = \frac{4\eta^2}{\pi\Gamma}\,\frac{n^2-1}{n^5}, \tag{2}$$

here ϵ_n and ϵ_∞, respectively, are the energy of the transition of the K-electron to one of the np-levels of the system and to the limit of the continuous spectrum, τ_n is the height of the n-absorption line, τ_∞ the height of the continuous spectrum, Γ the width of the absorption line and limit of the continuous spectrum. Ry is the Rydberg constant, n is the effective principal quantum number of the n-energy level, and η is the effective charge of the K-ionized absorbing atom in the molecule. The last of these formulas was obtained recently [9] as a result of a more rigid development than that in [7]; it was shown in [17] that it is quite justified when calculating spectra of many molecules in which the central symmetry of the field is preserved. An attempt, however, to use Eq. (2) directly to calculate the K-absorption edge of a metallic atom in molecules such as ferrocene brought on some difficulties, since the ratio τ_n / τ_∞ obtained experimentally turned out to be substantially greater than the one obtained from Eq. (2) by calculation [1]. Within the limits of a one-electron approximation it seemed natural to explain this fact by the effect of the molecular electrical field (in this case having the D_{5d} symmetry) on the hydrogen-like system, as it is formed after K-ionization of the central atom.

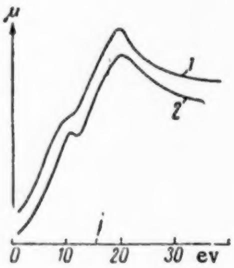

Fig. 1. X-ray absorption spectra of iron in $Fe(C_5H_5)_2$ (1) and in $Fe(C_5H_5)_2Cl$ (2).

The nature of all group D_{5d} notation not cited before is presented in Table 2. It can be seen, that the uneven rotation of that group is brought about by the conversion of the hexametric level. That means, that in the symmetry field under consideration the number of positions to which a 1s-electron can attach itself in the process of liberation during K-absorption has increased to six; as compared with the three p-position hydrogen-like system in fields of other symmetries or in the absence of an external field.

TABLE 2. Nature of Group D_{5d} Notation not Cited Before

	E	$C_5^{\pm 1}$	$C_5^{\pm 2}$	$5u_2$	I	$S_{10}^{\pm 1}$	$S_{10}^{\pm 3}$	$5\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1
A_{2g}	1	1	1	−1	1	1	1	−1
E_{1g}	2	$2\cos\frac{2\pi}{5}$	$2\cos\frac{4\pi}{5}$	0	2	$2\cos\frac{2\pi}{5}$	$2\cos\frac{4\pi}{5}$	0
E_{2g}	2	$2\cos\frac{4\pi}{5}$	$2\cos\frac{2\pi}{5}$	0	2	$2\cos\frac{4\pi}{5}$	$2\cos\frac{2\pi}{5}$	0
A_{1u}	1	1	1	1	−1	−1	−1	−1
A_{2u}	1	1	1	1	−1	−1	−1	1
E_{1u}	2	$2\cos\frac{2\pi}{5}$	$2\cos\frac{4\pi}{5}$	0	−2	$-2\cos\frac{2\pi}{5}$	$-2\cos\frac{4\pi}{5}$	0
E_{2u}	2	$2\cos\frac{4\pi}{5}$	$2\cos\frac{2\pi}{5}$	0	−2	$-2\cos\frac{4\pi}{5}$	$-2\cos\frac{2\pi}{5}$	0

If the distance between these levels is small (compared to the width of the K-position of the absorbing atom), then as its increase one can expect a doubling in the relative intensity of lines of selective x-ray absorption of the central atom in molecules of the type under study, when compared with those molecules in the field of which the mentioned "increase" in the levels does not occur. The difference between energy levels which capture 1s-electrons in the process of K-absorption should increase with increasing degrees of ionic bond strengths in molecules such as $Me(C_5H_5)_2$ and increasing field strength which acts on the central atom; together with this the width of selective absorption bands should increase. On the other hand, the intensity of those bands should decrease. For instance, for such practically ionic compounds as $Mn(C_5H_5)_2$ it should differ substantially from the value calculated according to formula (2). These conclusions have been backed up by analysis of all experimental material available at this time. Thus we assumed, when calculating the fine structure of absorption spectra of metal in bis-(cyclopentadienyl) complexes with typical covalent bonds (as for instance, ferrocene), that the increase of relative intensity of the selective absorption lines is close to the maximum.* In that case the calculation of spectra and the determination of energy

* In order to estimate errors, which can be introduced into the results due to insufficient exact knowledge of the correction factor in formula (2), we noticed that a 50% variation from the value selected by us (two) can , other conditions being equal, lead to an increase of 15% of the calculated atomic charge for iron in a molecule of ferrocene.

constants as they relate to the absorbing atom in such molecules can be accomplished without much trouble. Figures 2 and 3 show the results of such calculations of x-ray K-absorption spectra of iron in $Fe(C_5H_5)_2$* and $Fe(C_5H_5)_2Cl$. There is obvious good agreement with data obtained theoretically [1, 3].

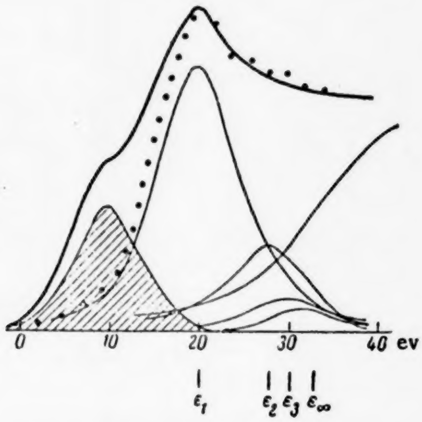

Fig. 2. Calculation of the fine structure of x-ray K-absorption spectra of iron in $Fe(C_5H_5)_2$. Heavy line: experimental curve; thin lines: lines of selective absorption and continuous edge; cross-hatched absorption band, connected with the transition of 1s-electrons to the molecular energy levels; the dots represent the theoretical summary absorption curves, due to the "exciton" type absorption.

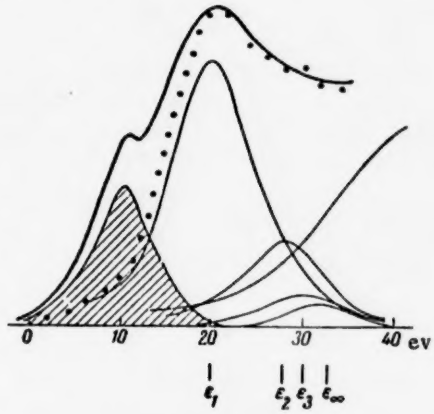

Fig. 3. Calculation of the fine structure of x-ray K-absorption spectra of iron in $Fe(C_5H_5)_2Cl$. Same notation as in Fig. 2.

The magnitudes of charges concentrated on iron atoms in both complexes in question practically (within the accuracy of their determination by x-ray spectroscopy) coincide and are close to +0.7, and two other parameters characterizing the position of the absorbing atom in the molecule are n = 1.75, Γ = 11.2 ev. This means, for instance, that in comparison with the x-ray spectrum of iron in $K_3Fe(CN)_6$ ($\eta' = \eta - 1 = 1$; n = 1.7 and Γ = 7.5 ev), in the spectra of ferrocene the selective absorption band width undergoes the greatest change, an increase to almost 50% at the cost of broadening of the final level of transition of the photoelectron in the molecule. In the x-ray absorption spectra of metals in aromatic complexes there is found, as could be expected from theoretical calculations, a rather intense band, together with a series of absorption bands of the "exciton" type; that band owes its appearance to the transitions of 1s-electrons of the absorbing atom to a group of molecular levels of similar symmetry. The width of these bands agrees well with what can be expected on the basis of analytical data (1) regarding the energies of corresponding molecular orbitals of complexes, and their relative intensity changes on transition from the spectrum of iron in ferrocene to that relating to the cation. In ferricinin it is 5% higher than the intensity of the molecular band in the spectrum of iron in a neutral molecule.

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* At the time of preparation of this work for printing, article [18] appeared, in which an analogous attempt to calculate x-ray K-absorption spectra of iron in ferrocene is reported, ferrocene having been obtained as in [13]. This checked out to be wrong.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

A CASE OF THE DISPLAY OF PSEUDOHALOID PROPERTIES BY A TRIFLUOROMETHYL GROUP ATTACHED TO A CARBON ATOM

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As is known, the perfluoroalkyl group possess strong electron affinity and its influence on the character of the molecule in many cases can be compared with the influence of halogens. These properties are most marked in the case of the trifluoromethyl group, this being in keeping with its high electronegativity (χ_{CF_3} 2.9-3.3), which lies between the electronegativity of fluorine (χ_F 4.0) and chlorine (χ_{Cl} 3.0).

Cases where the trifluoromethyl group behaves similarly to a halogen are widely known among perfluoroalkyl derivatives of elements: Hg [1-3]; Li [4], Mg, Zn, Cd [5]; Si [6]; P, As, Sb [7, 8]; S [9]; I [10]; and others. The most typical case is the hydrolysis of those compounds where the trifluoromethyl group is frequently quantitatively eliminated as fluoroform

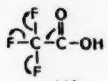
$$(CF_3)_n - X + nH_2O \rightarrow nCF_3H + X(OH)_n.$$

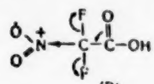
Much less study has been given to those instances where pseudohaloid properties are possessed by a perfluoroalkyl group bound to a carbon atom. The haloform decomposition of perfluoroketones is perhaps the sole authentic reaction of a similar nature [11]. However, compounds are known in which the CH_3-group, contrary to expectations, does not display pseudohaloid properties, as in trifluoroacetic acid, for instance.

As a result of the greater electronegativity of fluorine in comparison with chlorine, the trifluoromethyl group is more electrophilic than the trichloromethyl; however, trifluoroacetic acid is heat-stable and does not undergo haloform decomposition.

The only explanation of this fact lies in the strong electron-holding action of the three fluorine atoms, exceeding by far the similar action of chlorine, as a result of which the linkage of the carbonyl group to the fluorine atoms is made possible and the strengthening of the C−C bond in trifluoroacetic acid (A).

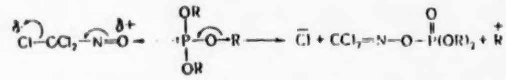
Thus, accumulation of strong electronegative substituents attached to the carbon atom in acetic acid leads at first to decrease in stability of the C−C bond and subsequently to its strengthening at the expense of the "reversible polarization" of the carbonyl oxygen. A further example of this is the unusual stability of difluoronitroacetic acid [12] (B).


(A)

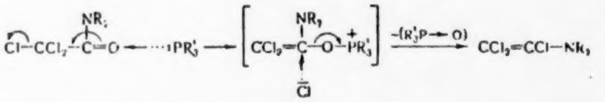

(B)

The possibility of "reversible polarization" of the carbonyl oxygen it would appear, contradicts the generally accepted view regarding its reactivity; however, attempts at observing a series of reactions from this viewpoint are quite worthwhile. As an illustration, the well-known Perkow [13] reaction for obtaining vinyl ethers of phosphoric acid may be considered, the mechanism of which can be treated as the nucleophilic attack of the free pair of electrons of the phosphorus atom on the positively charged (as a result of "reversible polarization") oxygen atom of the carbonyl group.

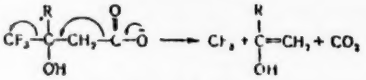
or the action of trichloronitrosomethane on triethylphosphite, leading to the formation of a derivative of dichloroformoxime [14]



Recently, an attempt was made to explain from the same viewpoint the preparation of trichlorovinylalkylamines from dialkylamides of trichloroacetic acid [15]



During a study of fluorinated β-hydroxy acids we have found a new and clear example of the manifestation of the pseudohaloid properties by a trifluoromethyl group attached to a carbon atom. On pyrolysis of the potassium salts of β,β-ditrifluoromethyl-β-hydroxypropionic (I) and β-trifluoromethyl-β-hydroxybutyric (II) acids, elimination of the trifluoromethyl and the carboxyl groups occurs, with formation of the corresponding ketones, trifluoroacetone and acetone.



I $R = CF_3$; II $R = CH_3$.

Special attention was given to the clarification of the fate of the trifluoromethyl anion, which can either lose a fluorine ion, thus being converted into difluorocarbene and then into tetrafluoroethylene

$$\bar{C}F_3 \rightarrow CF_2: + \bar{F};\quad 2CF_2: \rightarrow CF_2 = CF_2,$$

or react with the resulting acetone with formation of fluoroform

$$\bar{C}F_3 + RH \rightarrow CF_3H + \bar{R}.$$

It appears that the trifluoromethyl group is practically quantitatively converted into fluoroform.

On pyrolysis of the potassium salt of hydroxy acid I, another reaction course was observed, namely, a 30% yield of β,β-ditrifluoromethyl-β-propiolactone (III) was obtained, the properties of which had been studied by us previously [16]

It was also considered of interest to investigate the behavior of the trifluoromethyl group in salts of β,β-ditrifluoromethylacrylic (IV) and β-trifluoromethylcrotonic (V) acids.

On pyrolysis of the potassium salt of β,β-ditrifluoromethylacrylic acid its fluoroanhydride (VI) was obtained, identified as the anilide (VII)

$$\underset{(IV)}{(CF_3)_2C{=}CH{-}COOK} \xrightarrow{200°} \underset{(VI)}{(CF_3)_2C{=}CH{-}COF} \xrightarrow{C_6H_5NH_2} \underset{(VII)}{(CF_3)_2C{=}CH{-}CONHC_6H_5}$$

On thermal decomposition of the potassium salt of β-trifluoromethylcrotonic acid, a small yield of trifluoroisobutylene only was obtained.

Thus, a trifluoromethyl group attached to a carbon in the second valence state is immobile, similarly to "vinyl" chlorine. This fact can also be regarded as manifestation in it of pseudohaloid properties.

TABLE 1

Compound	Quantity, g	Temp. at onset of decomp. °C	Reaction products	Quantity, g yield, %	Mol. wt. found	Mol. wt. calc.	Constants	Data in lit.	Analysis, % found	Analysis, % calc.	Characterized by conversion into known
$(CF_3)_2C(OH)$—CH_2—COOK*	12,78	190	CF_3COCH_3	3,17 (59)			B.p. 21—25°				2,4-Dinitrophenylhydrazone
			$(CF_3)_2C$—CH_2 with O—CO (ring)	2,67 (26)			B. p. 90—94° n_D^{20} 1,3244	[16] B.p. 94,5—95° n_D^{20} 1,3240			Anilide of β,β-di-trifluoromethyl-β-hydroxypropionic acid [16]
$(CF_3)(CH_3)C(OH)$—CH_2—COOK	23,42	195—200	CF_3H	7,00 (91)	68,6	70	B. p. —81—(—79,5°)		C 17,14 H 1,43 F 81,41	17,14 1,34 81,42	
			CH_3COCH_3	4,22 (65)			B.p. 57—59°				2,4-Dinitrophenylhydrazone
$(CF_3)_2C$=CH—COOK	19,20	190—200	$(CF_3)_2CH$—CH=CH—COF	8,6 (52)			B.p. 64—65°/752mm n_D^{20} 1,3010 d_4^{20} 1,5275 found *MR* 25,78 calc. 25,82		C 28,60 H 0,49 F 63,34	28,55 0,48 63,35	Anilide of β,β-ditrifluoromethylacrylic acid [17]
$(CF_3)(CH_3)C$=CH—COOK	20,23	270	$(CF_3)(CH_3)C=CH_2$	2,62 (23)	110,4	110,0	B. p. 3,6—3,7°	[18] B. p. 6,4°	C 24,30 H 0,55 F 66,30	24,23 0,50 67,19	

* Pyrolysis was carried out in vacuo.

EXPERIMENTAL

Preparation of potassium salts of acids. The salts were readily obtained by neutralizing the acids with a small excess of dry bicarbonate followed by air-drying and recrystallizing from a suitable solvent. Properties of the salts obtained are given in Table 2.

TABLE 2

Compound		Solvent for recrystallization	M. p., °C	Analysis, %	
				found	calc.
I	$(CF_3)_2C(OH)-CH_2-COOK$	Reprecip. in the cold by CCl_4 from ethyl acetate	182	C 22,70 H 1,13 F 40,93	22,68 1,17 43,19
II	$(CF_3)(CH_3)C(OH)-CH_2-COOK$	The same	156–160 (decomp)		
IV	$(CF_3)_2C=CH-COOK$	Abs. dioxane	168		
V	$(CF_3)(CH_3)C=CH-COOK$	As for I	236–238	C 24,22 H 0,44	24,40 0,41

$$\underset{\text{(V)}}{(CF_3)(CH_3)C=CH-COOK} \xrightarrow{300^\circ} \underset{\text{(VIII)}}{(CF_3)(CH_3)C=CH_2}.$$

Thermal decomposition of salts. Pyrolysis of the dry salts was achieved by heating them in a pyrex flask on a metal bath. The reaction products were collected in a receiver cooled either to −78° or to −110°C. Gases were then distilled off from the high-boiling fraction on a Podbil'nyak column. The residue was fractionated on an ordinary column. Pyrolysis of salts was carried out in vacuo in ground-glass apparatus. The salt was placed in a test tube, which was then connected with the receiver fitted with a tap to evacuate the system. On reaching a vacuum of 0.05 mm Hg, the tap was turned off, the receiver cooled with liquid nitrogen and pyrolysis carried out. On completing of the reaction, the products were separated as in Expt. 1. Results of pyrolysis of salts are given in Table 1.

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THERMAL ALKYLATION OF CYCLOHEXANE BY OLEFINS UNDER PRESSURE

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Alkylation of aromatic, normal and isoparaffin hydrocarbons by olefins has been the subject of many investigations. The method mentioned for synthesis of isoparaffin and aliphatic – aromatic hydrocarbons has attained wide industrial use. On the other hand, alkylation of the important class of cycloparaffin hydrocarbons has remained almost completely unstudied up to the present time.

Pines and Ipatieff [1] investigated the alkylation of methylcyclopentane in the presence of 100% H_2SO_4 and HF by butylenes, isobutylene, pentene-1, and other olefins. The process proceeded in a very complex manner, and direct combination products of the olefins were not obtained. The occurrence of alkylation could be judged only by observing possible intermediate reactions – isomerization of resulting dialkylcyclopentane into dialkylcyclohexane and migration of an alkyl group. Mamedaliev with Kuliev [2] and with Mamedova [3] alkylated methyl-, ethyl-, and isopropylcyclohexanes with propylene and butylene in the presence of H_2SO_4. In this instance, substituded cyclohexanes were obtained with side alkyl groups corresponding to the original olefin. However, unsubstituted cyclohexane and cyclopentane were not alkylated under these conditions and monoalkylcyclanes could not be obtained by this method.

In the present work, direct alkylation of cyclohexane with ethylene, propylene, and isobutylene at elevated temperatures and pressures has been accomplished for the first time. The basic reaction products have been isolated and characterized, and the influence of a series of factors on the reaction course studied.

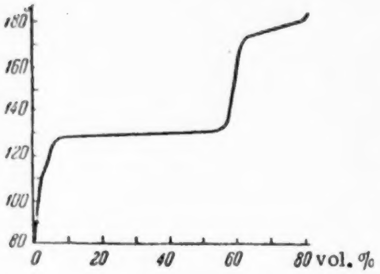
EXPERIMENTAL

Experiments were carried out in apparatus of a recirculating type, similar to that described previously [4]. Pressure in the reactor was produced by the reaction mixture, withdrawn from the mixing vessel by a liquid fluid pump. Into a 120 ml reactor were placed 50 ml of $Ca_3(PO_4)_2$ and 70 ml of porcelain chips or 120 ml of quartz fragments. The cyclohexane had b. p. 80.3°, $n^{20.5}D$ 1.4266, and d^{20}_4 0.7752. The resulting catalyzate was fractionated on a high-efficiency column. The homogeneous fractions from several experiments were united and investigated. Separation of impurities in the unsaturated hydrocarbons and isolation of aromatic hydrocarbons was effected by chromatography on a silica gel. The structure of the alkylcyclohexanes obtained was determined by converting them by dehydrogenation over a Pt/C (20% Pt) catalyst at 300° into the corresponding aromatic hydrocarbons and oxidation of the latter into acids.

Alkylation with ethylene. In experiments at 200 and 450 atm pressure (450°) ethylene used in the reaction was fully absorbed, and at 100 atm – to the extent of 90%. After removal of cyclohexane from the alkylate, two fractions were isolated: I – of monoethylcyclohexane (b. p. 129-131°), II – of diethylcyclohexane (b. p. 170-185°), and a higher-boiling residue, (see the figure). After isolation from unsaturated products, 27 ml of a product with $n^{20}D$ 1.4323 and d^{20}_4 0.7857 was obtained from 30 ml of fraction I. According to [5], for ethylcyclohexane: b. p. 131.78°, $n^{20}D$ 1.4378, d^{20}_4 0.7879. After its dehydrogenation and subsequent chromatography, ethylbenzene with $n^{20}D$ 1.4957, d^{20}_4 0.8660 was obtained. According to [5] for ethylbenzene $n^{20}D$ 1.4959, d^{20}_4 0.8670. By Ullmann oxidation, benzoic acid with m. p. 122.5° was obtained from it.

After removal of unsaturated products (28%) from fraction II, it distilled completely at 172-175° and had $n^{20}D$ 1.4415, d^{20}_4 0.8013. These properties are close to the properties of the isomeric diethylcyclohexanes. After

dehydrogenation and subsequent chromatography, a narrow fraction of hydrocarbons (80%) with b. p. 178-180°/740 mm, $n^{20}D$ 1.4918, d^{20}_4 0.8613, was obtained from the catalyzate. These properties correspond to the isomers of diethylbenzene [5]. On a chromatogram of the diethylbenzene obtained (with dibutyl sebacinate as the carrier) two peaks were observed. Diethylbenzene was oxidized according to [6] into a mixture of phthalic acids, from which, utilizing their differing solubility in hot water [7], were isolated the individual acids: O-phthalic, iso-phthalic, and terephthalic – in the proportions by weight of 1 : 1.6 : 8. On sublimation of the o-isomer, acicular crystals of the anhydride were formed.



Alkylate fractionation curve in Expt. No. 3.

Under optimum conditions (Expt. 3) 212 g of cyclohexane was recovered from the 253 g used in the reaction. Besides fractions of mono- and diethylcyclohexane, constituting the main part of the alkylate (50 and 20% respectively), was isolated also a small amount (3.2%) of low-boiling products (with b. p. up to 75°) resulting from cracking and dimerization of an olefin, the products not being investigated by us. The remaining portion of the alkylate corresponded to the intermediate fraction portion (85-125° and 135-170°) and the high-boiling residue. The residue, 75% of which was distributed among the fractions: b. p. 185-220°, $n^{20}D$ 1.4570, d^{20}_4 0.8262, and b. p. 220-250°, $n^{20}D$ 1.4640, d^{20}_4 0.8393, was evidently a mixture of polyethylcyclohexanes. In Expt. 3 in Table 1 was included 11% of unsaturated hydrocarbons, the major portion of which corresponded to the intermediate fractions and the residue. The monoethylcyclohexane fraction contained 3.4%, and the diethylcyclohexane fraction 13% of unsaturated hydrocarbons, the nature of which was not studied.

TABLE 1

Prep. No.	Experimental conditions *			Yield of alkylate on ethylene used, %	Content in alkylate, wt. %		
	pressure atm	cyclohexane: ethylene, moles	rate of passing mixture, ml/min		of monethylcyclohexane fraction	of diethylcyclohexane fraction	of residue
1	100	3.0	1.6	89	34	14	26
2	200	3.0	0.3	225	46	–	–
3	200	3.9	1.5	240	51	20	20
4	450	3.0	0.5	230	50	–	–
5	200	1.2	1.7	150	34	16	32
6	200**	2.0	0.6	176	28	9	44
7	200	2.1	3.3	220	27	16	38
8	200	4.4	3.4	230	41	20	26

* 1-6 were carried out with $Ca_3(PO_4)_2$; 7, 8 in the presence of quartz.

** At 400°.

From Table 1 it is seen (experiments carried out at 450°) that on increasing ethylene concentration in the initial mixture, monethylcyclohexane yield was lowered, and yield of high-boiling residue increased. A similar effect was shown by decreasing rate of passing the mixture.

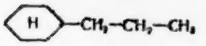
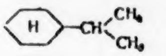
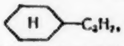
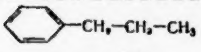
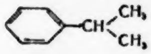
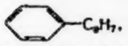
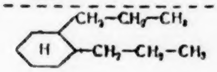
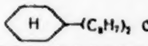
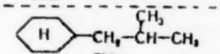
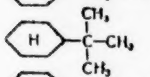
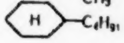
Alkylation with propylene. A propylene – propane fraction containing 13% propane was used. From Table 2 it is seen that at 200 atm extent of propylene conversion (30%) and alkylate yield (93-96%) were significantly lower than with ethylene. At 450 atm and 500° extent of propylene conversion and alkylate yield increased. From the alkylates by distillation were isolated: a low-boiling fraction I of cracking products, a fraction II with b. p. 150-157°, and a residue. After removal of unsaturated products (5%), fraction II had: $n^{20}D$ 1.4370, d^{20}_4 0.7929. According to [5], for n-propylcyclohexane: b. p. 156.72°, $n^{20}D$ 1.4370, d^{20}_4 0.7936. After dehydrogenation over Pt/C, by distillation and chromatography a product was obtained (48%) with b. p. 158.2-158.5°, $n^{20}D$ 1.4903, d^{20}_4 0.8612. According

to [5], for n-propylbenzene: b. p. 159.22°, $n^{20}D$ 1.4920, d^{20}_4 0.8620. From the residue by distillation and chromatography on a silica gel was obtained a hydrocarbon with b. p. 209-211°/739 mm, $n^{20}D$ 1.4481, d^{20}_4 0.8102, the weight of which constituted about 30% of the weight of the residue. These properties are close to the properties of di-n-propylcyclohexane. According to [8], for the 1,2-isomer: b. p. 214.7-215°, $n^{20}D$ 1.4510, d^{20}_4 0.8188, and for the 1,4-isomer: trans – b. p. 220°, $n^{20}D$ 1.4440, d^{20}_4 0.8030; cis – b.p. 221°, $n^{20}D$ 1.4480, d^{20}_4 0.8138 [9].

TABLE 2

Prep. No.	Temp. °C	Experimental conditions			Degree of olefin conversion, %	Alkylate yield on olefin used, %	Content in alkylate, weight, %	
		pressure, atm	cyclohexane : : olefin, moles	rate of passage of mixture, hr^{-1}			of monoalkylcyclohexane fraction	of residue
Alkylation with propylene								
9	450	200	2,8	1,60	32	96	28	51
10	450	200	3,7	1,45	30	93	41	45
11	500	450	3,0	1,20	70	206	31	56
12	500	450	5,0	1,45	70	180	53	34
Alkylation with isobutylene								
13	450	200	1,9	1,17	—	85	39	35
14	450	450	3,0	1,19	—	180	44	38
15	450	450	2,7	1,31	31	150	42	38

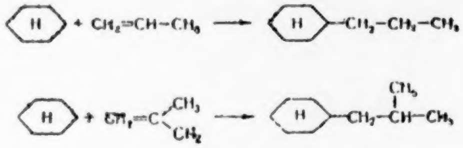
TABLE 3

Hydrocarbons	B. p., °C	d^{20}_4	n^{20}_D
	156,72	0,7936	1,4370
	154,56	0,8022	1,4409
 obtained by us	155—156	0,7929	1,4370
	159,22	0,8620	1,4920
	152,39	0,8618	1,4915
 obtained by us	158,2—158,5	0,8612	1,4903
	214,7—215,0	0,8188	1,4510
 trans-cis	220	0,8030	1,4440
	221	0,8138	1,4480
 obtained by us	209—211 (739 mm)	0,8102	1,4481
	171,32	0,7952	1,4386
	171,59	0,8127	1,4469
 obtained by us	171—172 (742 mm)	0,7942	1,4393

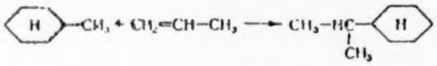
By comparing the results of Expts. 9 and 11 on quartz and 10 and 12 on $Ca_3(PO_4)_2$ it is seen that in the presence of phosphate, monopropylcyclohexane content in the alkylate is higher and that of the di- and polysubstituted compounds lower.

Experiments with isobutylene were carried out in the presence of quartz. Degree of conversion of isobutylene was lower than that of propylene. From the alkylate by distillation was isolated a fraction with b. p. 168-183°. After separation from unsaturated products (bromine value 11-12) and distillation a hydrocarbon (57%) was obtained from it with b. p. 171-172°/742 mm, $n^{20}D$ 1.4393, d^{20}_4 0.7942. According to [5], for isobutylcyclohexane b. p. is 171.32°, $n^{20}D$ 1.4386, d^{20}_4 0.7952.

In Table 3 are shown the constants for hydrocarbons of normal and iso structure, taken from [5] and prepared by us. From Table 3 it is seen that the constants for the propylbenzene obtained are near to the constants of the hydrocarbon with normal side chain. Constants for the butylcyclohexane obtained are near to the constants of isobutylcyclohexane. Thus, in both cases cyclohexane evidently combines with the outer unsaturated C- atom of the olefin:



As distinct from this, in acidic alkylation of methylcyclohexane with propylene methylisopropylcyclohexane was obtained [3], i.e., the cyclane combined with the central unsaturated C-atom of the olefin:



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ADDITION OF TRICHLOROBROMOMETHANE TO COMPOUNDS OF THE STRUCTURE $R(C_6H_5)_2ECH = CH_2$ (where $R = C_6H_5$; E = Sn, Si, C)

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In recent years a detailed study has been made of the regrouping of radicals in solution with 1,2- migration of phenyl from one carbon atom to another (see, for instance [1]) according to the scheme

$$C_6H_5CR_1R_2\dot{C}HR_3 \rightarrow \dot{C}R_1R_2CHR_3C_6H_5,$$
$$R_1 = CH_3,\ Ar;\ R_2 = CH_3,\ Ar;\ R_3 = H,\ CH_3.$$

Similar regrouping with 1,2-migration of phenyl from an atom of a metal to a carbon atom is unknown.

The present work is devoted to the study of the ability to regroup in solution of radicals of structure

$$(C_6H_5)_3Sn\dot{C}HCH_2CCl_3,\ (C_6H_5)_3Si\dot{C}HCH_2CCl_3,\ (C_6H_5)_2\underset{\displaystyle CH_3}{\underset{|}{C}}\dot{C}HCH_2CCl_3.$$

With this in view, the addition of trichlorobromomethane to vinyltriphenylstannane,* vinyltriphenylsilane,** and 3,3-diphenylbutene-1*** was studied. 3,3-Diphenylbutene-1 was chosen for investigation because of its greater availability compared with vinyltriphenylmethane.

Addition of trichlorobromomethane to vinyltriphenylstannane and vinyltriphenylsilane proceeds very smoothly and regrouping products of the addition are formed in almost quantitative yield according to the scheme.

$$(C_6H_5)_3ECH = CH_2 + BrCCl_3 \xrightarrow{Bz_2O_2} (C_6H_5)_3ECHBrCH_2CCl_3.$$

The composition of the products was confirmed by the absence of an E-Br**** bond (negative test with $AgNO_3$, etc.), and also by the behavior of the adducts obtained toward the action of alcoholic alkali. The organotin compound does not hydrolyze, and undergoes dehydrobromination according to the scheme

$$(C_6H_5)_3SnCHBrCH_2CCl_3 \xrightarrow{KOH} (C_6H_5)_3SnCH = CHCCl_3.$$

The organosilicon compound, as would be expected of an α-haloidalkylsilane [5], is inert to the action of alcoholic alkali at room temperature.

* Preparation of the addition product of trichlorobromomethane to vinyltriethylstannane has been briefly reported [2], but the adduct's composition has not been investigated.

** Addition of chloroform and carbon tetrachloride to vinyltriphenylsilane has been described [3]; in these cases compounds of composition $(C_6H_5)_3Si(CH_2)_2CCl_3$ and $(C_6H_5)_3SiCHClCH_2CCl_3$ were obtained.

*** Homolytic addition of n-butyl mercaptan and thioacetic acid to 3,3-diphenylbutene-1 leads to unregrouped products; addition of n-butyraldehyde proceeds with regrouping in the radical formed as an intermediate with 1,2-migration of phenol [4].

**** Where regrouping occurs, formation of a compound of composition $(C_6H_5)_2EBrCH(C_6H_5)CH_2CCl_3$ would be expected.

Addition of trichlorobromomethane to 3,3-diphenylbutene-1 proceeds with difficulty. After boiling the reaction mixture for 20 hr with repeated addition of peroxide, 66% of the initial diphenylbutene is recovered in the unchanged form. The chief reaction product is an unsaturated compound of composition $C_{17}H_{15}Cl_3$. On ozonolysis of this compound, formaldehyde and a ketone of composition $C_{16}H_{13}Cl_3O$ are obtained, the latter giving a 2,4-dinitrophenylhydrazone of composition $C_{22}H_{17}Cl_3N_4O_4$. In this case, if the reaction being studied proceeds without regrouping, formation of an unsaturated compound of structure I or II would be expected:

$$\underset{\text{I}}{(C_6H_5)_2C(CH_3)CH=CHCCl_3},\quad \underset{\text{II}}{(C_6H_5)_2C(CH_3)\overset{CCl_3}{\overset{/}{C}}=CH_2}.$$

In a reaction involving regrouping, formation of compounds III and IV would be expected:

$$\underset{\text{III}}{CH_2=C(C_6H_5)CH(C_6H_5)CH_2CCl_3},\quad \underset{\text{IV}}{CH_3-\underset{C_6H_5}{C}=\underset{C_6H_5}{C}-CH_2-CCl_3}$$

The data given above, characterizing the compounds obtained, is consistent with formula III only.

Compounds I and IV cannot lead to formation of formaldehyde and the ketone indicated on ozonolysis. Formation of compound II is exceedingly unlikely, since addition of a CCl_3-radical would be needed, this being contrary to the known rules of orientation. In addition, although compound II is also capable of forming formaldehyde and a ketone of composition $C_{16}H_{13}Cl_3O$ on ozonolysis, the ketone obtained in this case would have the structure $(C_6H_5)_2C(CH_3)COCCl_3$ and, consequently, could not give a 2,4-dinitrophenylhydrazone of composition $C_{22}H_{17}Cl_3N_4O_4$, since it is known [6] that carbonyl compounds possessing the grouping $CCl_3\overset{|}{C}=O$ on reacting with dinitrophenylhydrazine in the presence of sulfuric acid give hydrazones containing no chlorine.

Formation of substance III during the reaction studied could be described by the scheme

$$CH_3C(C_6H_5)_2CH=CH_2+\dot{C}Cl_3\rightarrow CH_3C(C_6H_5)_2\dot{C}HCH_2CCl_3$$
$$\xrightarrow{\text{Rearrangement}} CH_3\dot{C}(C_6H_5)CH(C_6H_5)CH_2CCl_3 \xrightarrow{BrCCl_3} \dot{C}Cl_3+HBr+CH_2=C(C_6H_5)CH(C_6H_5)CH_2CCl_3$$

Simultaneously with substance III is obtained in small yield a saturated adduct, the structure of which has not been investigated. Thus, under comparable conditions, radicals of structure $(C_6H_5)_3E\dot{C}HCH_2CCl_3$ (E = Sn, Si) did not regroup, but radicals of structure $(C_6H_5)_2C(CH_3)\dot{C}HCH_2CCl_3$ did regroup. A possible cause of this difference could be either the lower stability of radicals of the type $(C_6H_5)_2\dot{E}CH(C_6H_5)CH_2CCl_3$ compared with the initial radicals $(C_6H_5)_3E\dot{C}HCH_2CCl_3$, or that tin and silicon atoms are less capable of transmitting the effect occasioned by the presence of an odd electron on the carbon atom adjacent to the phenyl group.

EXPERIMENTAL

Addition of trichlorobromomethane to vinyltriphenylstannane in the presence of benzoyl peroxide. A solution of 9.42 g (0.025 mole) of vinyltriphenylstannane (obtained as in [7]), 10 g of trichlorobromomethane, and 0.15 g of benzoyl peroxide was heated on a water bath at a temperature of 80° for 7 hr. After this time, a further 0.15 g of benzoyl peroxide in 10 g of trichlorobromomethane was added to the reaction solution. After distillation of excess trichlorobromomethane, 14.3 g of a viscous oil remained, from which, by solution in absolute alcohol and cooling to −40°, was obtained γ,γ,γ-trichloro-α-bromopropyltriphenylstannane as crystals with m. p. 58-60°, yield 13.5 g (94% theoretical); after recrystallizing from alcohol, m. p. was 61-62°.

Found %: C 43.76, 43.58; H 3.15, 3.20. $C_{21}H_{18}SnCl_3Br$. Calculated %: C 44.02; H 3.15.

The product did not react with potassium fluoride, silver nitrate, nor did it form a complex compound with pyridine.

Reaction of γ,γ,γ-trichloro-α-bromopropyltriphenylstannane with alkali. To a solution of 4.80 g (0.008 mole) of γ,γ,γ-trichloro-α-bromopropyltriphenylstannane in 120 ml of ethyl alcohol cooled to 0° was added 0.45 g

(.008 mole) of caustic potash in 16 ml of ethyl alcohol. The reaction mixture was left overnight at room temperature. Neutralization was then complete. Crystals of γ,γ,γ-trichloropropen-1-yltriphenylstannane precipitated, which after recrystallizing twice from alcohol had m. p. 132°. Yield 3.35 g (80% theoretical).

Found %: C 50.33, 50.31; H 3.41, 3.41; Sn 23.73, 23.72. $C_{21}H_{17}SnCl_3$. Calculated %: C 50.90; H 3.44; Sn 24.00.

Addition of trichlorobromomethane to vinyltriphenylsilane in the presence of benzoyl peroxide. A solution of 7.15 g (0.025 mole) of vinyltriphenylsilane (obtained as in [8]), 10 g of trichlorobromomethane, and 0.15 g of benzoyl peroxide was heated on a water bath at 80° for 7 hr. After this time to the reaction solution was added a further 0.15 g benzoyl peroxide in 10 g of trichlorobromomethane.

After distillation of excess trichlorobromomethane, 11.9 g of an oil was obtained, readily soluble on ether and benzene. After crystallization from alcohol, 11.3 g (94.1% theoretical) of γ,γ,γ-trichloro-α-bromopropyltriphenylsilane was obtained with m. p. 98-102°. After a second recrystallization from alcohol, m. p. was 102-103°.

Found %: C 52.09, 52.00; H 3.72, 3.71; Si 5.87, 5.72; Hal 38.43, 38.69. $C_{21}H_{18}SiCl_3Br$. Calculated %: C 52.03; H 3.74; Si 5.74; Hal 38.39.

The product did not react with silver nitrate solution, and also remained unchanged on reacting with alcoholic alkali for 20 hr at room temperature.

3,3-Diphenylbutene-1. Synthesis was achieved according to the scheme given in [4],* the product having constants: b. p. 92-94° at 1 mm, $n^{25}D$ 1.5770, $n^{20}D$ 1.5790, d^{20}_4 1.0106. MR found 68.49. MR calculated for $C_6H_{16}F_7$ 68.42. Data in the literature [4]: b. p. 111-115° at 1.5 mm, $n^{25}D$ 1.5780. A solution of 2.5 g of 3,3-diphenylbutene-1 in 100 g of carbon tetrachloride after cooling with ice was saturated with 6% ozone for 3 hr. After addition of water, carbon tetrachloride was distilled off in vacuo, after which the ozonide was decomposed by heating on a boiling water bath. By extracting with ether, 2.1 g (84% theoretical) of α,α-diphenylpropionaldehyde was obtained with b. p. 111-113° at 1 mm, $n^{20}D$ 1.5820, d^{20}_4 1.0810. MR found 64.85. MR calculated for $C_{15}H_{14}OF_6$ 64.25. According to the data in the literature [9], b. p. of α,α-diphenylpropionaldehyde is 111-113° at 1 mm, $n^{20}D$ 1.5800. From the aqueous layer was obtained a dimedon derivative with m. p. 189°, giving no melting point depression when mixed with the dimedon derivative of formaldehyde. This confirmed the structure of the initial 3,3-diphenylbutene-1.

Reaction of trichlorobromomethane with 3,3-diphenylbutene-1 in the presence of benzoyl peroxide. A solution of 25 g (0.12 mole) of 3,3-diphenylbutene-1, 100 g of trichlorobromomethane, and 0.4 g of benzoyl peroxide was boiled for 20 hr; every 3 hr a 0.4 g amount of benzoyl peroxide was added. In all, 3 g of peroxide was added in 20 hr. 15-20 minutes after heating commenced, evolution of hydrogen bromide began. On completion of the reaction, the mixture was washed with soda solution, then with water, dried over magnesium sulfate, and excess trichlorobromomethane distilled off. By distilling the residue, the following were obtained:

Fraction I. 92-94° (1 mm), 15 g, $n^{25}D$ 1.5770. (initial substance).

Fraction II. 94-180° (1 mm), 10.5 g. Residue 3 g.

After a second distillation of fraction II at 1 mm were obtained:

Fraction I. 92-95°, 1.5 g, $n^{25}D$ 1.5770.

Fraction II. 95-142°, 0.5 g.

Fraction III. 142-150°, 6.5 g.

Fraction IV. 160-170°, 1 g. Residue 1 g.

After a second distillation of fraction III, 4.5 g of 5,5,5-trichloro-2,3-diphenylpentene-1 was obtained, b. p. 142-142.5° at 1 mm, $n^{20}D$ 1.5935, d^{20}_4 1.2437. MR found 88.74. MR calculated for $C_{17}H_{15}Cl_3F_7$ 87.64.

As shown by analysis, the substance obtained contained a trace of saturated bromide.

Found %: C 61.50; H 4.65; Hal 34.04. $C_{17}H_{15}Cl_3$. Calculated %: C 62.69; H 4.64; Hal 32.66.

* In contrast to the reference, the product obtained after decomposition of xanthogenate was subjected, without preparatory distillation, to heating with 5% aqueous alkali for 2 hr. After distillation of the product, treatment with alkali was repeated, whereupon 3,3-diphenylbutene-1 was obtained in 72.5% theoretical yield (in the reference, 50.7% theoretical).

A solution of 2.6 g of 5,5,5-trichloro-2,3-diphenylpentene-1 in 100 g of carbon tetrachloride after cooling with ice was saturated with 6% ozone for 4 hr. After addition of water, CCl_4 was distilled off in vacuo. The ozonide was decomposed by heating on a boiling water bath. By extracting with ether 2.3 g (88.5% theoretical) of white crystals with m. p. 106° was obtained.

Found %: C 58.77, 58.42; H 4.06, 4.09; Cl 32.67, 32.77. $C_{16}H_{13}Cl_3O$. Calculated %: C 58.65; H 4.00; Cl 32.47.

With 2,4-dinitrophenylhydrazine these crystals formed a 2,4-dinitrophenylhydrazone with m. p. 161° (from alcohol).

Found %: C 51.71, 51.94; H 3.55, 3.65; N 10.72, 10.77. $C_{22}H_{17}N_4Cl_3O_4$. Calculated %: C 52.03; H 3.38; N 11.03.

From the aqueous layer was obtained a dimedon derivative with m. p. 189°, giving no melting point depression when mixed with the dimedon derivative of formaldehyde.

From fraction IV by solution in a small amount of ether and cooling, crystals of a saturated addition product with m. p. 108° were obtained.

Found %: C 50.60, 50.36; H 4.02, 4.04; Hal 45.85, 45.73. $C_{17}H_{16}Cl_3Br$. Calculated %: C 50.22; H 3.96; Hal 45.83.

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HOMOLYTIC ISOMERIZATION OF 2-BROMO-3,3-DICHLOROBUTENE-1

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As has been shown previously, 2-bromo-3,3,3-trichloropropene after a certain induction period or on exposure to u.v. light isomerizes into 3-bromo-1,1,2-trichloropropene-1. This conversion has been interpreted as the result of homolytic regrouping [1].

In the present work, the susceptibility to isomerization of 2-bromo-3,3-dichlorobutene-1 was investigated, this compound being prepared according to the scheme

$$CH_3CCl_2-CH_2CH_2Br \xrightarrow{KOH} CH_3CCl_2CH=CH_2,$$
$$CH_3CCl_2-CH=CH_2 \xrightarrow[(CH_3COOH)]{Br_2} CH_3CCl_2CHBr-CH_2Br,$$
$$CH_3CCl_2-CBrH-CH_2Br \xrightarrow{KOH} CH_3CCl_2CBr=CH_2.$$

On standing or on exposure to u.v. light, a sample of the compound $CH_3CCl_2CBr=CH_2$ isomerizes into $CH_3CCl=CCl-CH_2Br$, which with thiourea forms a derivative containing no bromine, and isolated as the picrate. This isomerization can be illustrated by scheme (A), which is very similar to the scheme for the regrouping of 2-bromo-3,3,3-trichloropropene [1]:

$$CH_3CCl_2-CBr=CH_2 \xrightarrow{Br} CH_3CCl_2-\dot{C}Br-CH_2Br,$$
$$CH_3CCl_2\dot{C}Br-CH_2Br \xrightarrow{\text{regrouping}} CH_3\dot{C}Cl-CClBr-CH_2Br, \quad (A)$$
$$CH_3\dot{C}Cl-CClBr-CH_2Br \rightarrow CH_3CCl=CCl-CH_2Br + Br \text{ etc.}$$

Hydroquinone addition hinders such isomerization. Under the influence of $SbCl_5$ $CH_3CCl_2CBr=CH_2$ undergoes anionotropic allyl regrouping according to the scheme

$$CH_3CCl_2CBr=CH_2 \xrightarrow{SbCl_5} CH_3CCl=CBr-CH_2Cl.$$

2-Bromo-1,3-dichlorobutene-2 was isolated as the picrate of the isothiouronic derivative.

The structure of $CH_3CCl_2CBr=CH_2$ was confirmed by preparation of the dimethylamine derivative $CH_3CCl=CBr-CH_2N(CH_3)_2$, identified as the picrate. This amine, $CH_3CCl=CBr-CH_2N(CH_3)_2$, was obtained by two methods: reacting excess dimethylamine with 1,2-dibromo-3,3-dichlorobutane according to the scheme

$$CH_3CCl_2CHBr-CH_2Br \rightarrow CH_3CCl=CBr-CH_2N(CH_3)_2$$

and by reacting 2,3-dibromo-1,3-dichlorobutane, obtained by brominating $CH_3CCl=CH-CH_2Cl$, with dimethylamine.

The reaction of hydrogen bromide with $CH_3CCl_2CBr=CH_2$ in the presence of benzoyl peroxide was further studied. A mixture of isomers of structure $CH_3CCl=CCl-CH_2Br$ was obtained in 90% yield as the sole reaction product. The reaction indicated probably proceeds according to a scheme similar to (A). In the case in question, hydrogen bromide is the source of the bromine atoms initiating homolytic isomerization.

From a mixture of $CH_3CCl=CCl-CH_2Br$ by reacing with dimethylamine, amines $CH_3CCl=CCl-CH_2N(CH_3)_2$ were obtained, and isolated as the picrates, which contain no bromine, this confirming the indicated structure for the dichlorobromobutene. In all the reactions cited above, in which are formed unsaturated compounds of structure

$CH_3CCl=CX-CH_2Y$, where X = Cl or Br, Y = Br or $N(CH_3)_2$, manifestation of cis-trans-isomers was noted. But in the present work the stereochemistry of these reactions was not studied more closely.

Thus, substances of structure $XCCl_2-CBr=CH_2$, where X is Cl [1], CH_3, under the influence of radical agents undergo homolytic isomerization into $XCCl=CCl-CH_2Br$, accompanied by 1,2-migration of chlorine into the radicals formed as in intermediates:

$$\underset{1}{XCCl_2-\dot{C}Br-CH_2Br} \rightarrow \underset{2}{X\dot{C}Cl-CClBr-CH_2Br.}$$

Radicals of structure 2 are stabilized with formation of unsaturated $XCCl=CCl-CH_2Br$, this evidently being connected with the ease of splitting a Br atom from a system of the form $>\dot{C}-\underset{\displaystyle Br}{\underset{|}{C}}<$.

EXPERIMENTAL

1. Preparation of 3,3-dichlorobutene-1. 135 g of 1-bromo-3,3-dichlorobutane was dehydrobrominated with 45.9 g of KOH in ethyl cellosolve on mixing at 0°. After the usual treatment, on fractional distillation 35.5 g (43% theoretical) of 3,3-dichlorobutene-1 was obtained; b. p. 45° at 105 mm, $n^{20}D$ 1.4460, d^{20}_4 1.1043; MR found 30.16, calculated 29.94.

Found %: C 38.25, 38.44; H 4.96, 4.76. $C_4H_6Cl_2$. Calculated %: C 38.43; H 4.84.

On heating with thiourea for several minutes in alcoholic solution, the thiourea derivative was obtained as the picrate.

$$CH_3CCl=CH-CH_2-S-C\begin{matrix}\nearrow NH\\ \searrow NH_2\end{matrix}\cdot C_6H_3N_3O_7$$ with m. p. 168.5-170° (from alcohol)

Found %: C 33.33, 33.56; H 3.19, 3.14; N 17.74, 17.60. $C_{11}H_{12}ClN_5O_7S$. Calculated %: C 33.55; H 3.07; N 17.78.

A sample mixed with the picrate of the isothiourea derivative obtained from $CH_3CCl=CH-CH_2Cl$, gave no melting point depression.

2. Bromination of 3,3-dichlorobutene-1. To 90 g of $CH_3CCl_2CH=CH_2$ in 100 ml of glacial acetic acid 34.2 ml of bromine was added dropwise. After the usual treatment, 1,2-dibromo-3,3-dichlorobutane was fractionally distilled over the range 79-80° at 4 mm, weight 158 g (77% theoretical); $n^{20}D$ 1.5435, d^{20}_4 1.9810; MR found 45.35, calculated 45.94.

Found %: C 16.77, 17.00; H 2.08, 2.18. $C_6H_4Br_2Cl_2$. Calculated %: C 16.52; H 2.12.

On treatment with excess diemthylamine the unsaturated amine $CH_3CCl=CBr-CH_2N(CH_3)_2$ was obtained, distilling over the range 82-87° at 20 mm, $n^{20}D$ 1.4996-1.5006. Picrates were prepared with m. p. 153-154° (from alcohol). Found %: N 12.62, 12.68. M. p. found 160-161°.

Found %: N 12.62, 12.82. $C_{12}H_{14}BrClN_4O_7$. Calculated %: N 12.68 (compare with experiment 4).

3. Preparation of 2-bromo-3,3-dichlorobutene-1 and its properties. 127 g of 1,2-dibromo-3,3-dichlorobutane was dehydrobrominated with 34.2 g of KOH in ethyl cellosolve similar to Expt. 1. On fractional distillation 58 g (59% theoretical) of 2-bromo-3,3-dichlorobutene-1 was obtained with b. p. 61-62° at 25 mm, $n^{20}D$ 1.5120, d^{20}_4 1.6363; MR found 37.88, calculated 37.70.

Found %: C 24.00, 23.82; H 2.53, 2.44. $C_4H_5BrCl_2$. Calculated %: C 23.56; H 2.47.

On standing without addition of hydroquinone, the substance became lachrymatory, $n^{20}D$ 1.5300; with hydroquinone it did not isomerize. 2-Bromo-3,3-dichlorobutene-1, previously distilled ($n^{20}D$ 1.5130), was subjected to u.v. radiation. After 10 min $n^{20}D$ was 1.5280; after a further 20 min $n^{20}D$ was 1.5320. The substance distilled over the range 77-80° at 25 mm; $n^{20}D$ 1.5340, d^{20}_4 1.6674; MR found 38.01, calculated 37.70.

The picrate of the isothiourea derivative melted at 194.5-195° (from alcohol).

Found %: C 30.47, 30.73; H 2.55, 2.77; N 16.54, 16.54. $C_{11}H_{11}Cl_2N_5O_7S$. Calculated %: C 30.85; H 2.59; N 16.35.

On treatment of 2-bromo-3,3-dichlorobutene-1 with $SbCl_5$ an isomer was obtained which distilled over the range 75-80° at 24 mm, $n^{20}D$ 1.5380, from which by reacting with thiourea was obtained an isothiourea derivative as the picrate with m. p. 185° with decomposition (from alcohol).

Found %: C 28.44, 28.55; H 2.33, 2.52. $C_{11}H_{11}ClBrN_5O_7S$. Calculated %: C 27.95; H 2.35.

4. Reaction of 2-bromo-3,3-dichlorobutene-1 with dimethylamine. a) A solution of 7.9 g of 2-bromo-3,3-dichlorobutene-1, prepared as described in Expt. 3, in 20 ml of alcohol was heated in a sealed ampoule with excess dimethylamine for several hours at 100°. After the usual treatment, dimethyl-2-bromo-3-chlorobutene-2-yl-amine distilled at 81-83° at 20 mm, 5.6 g (68% theoretical); $n^{20}D$ 1.4994, d^{20}_4 1.3507; MR found 46.23, calculated 46.01. M. p. of picrate was 153-154° (from alcohol).

Found %: C 32.60, 32.84; H 3.13, 3.19; N 12.81, 13.00. $C_{12}H_{14}BrClN_4O_7$. Calculated %: C 32.66; H 3.19; N 12.68.

A sample of this picrate mixed with a sample of the corresponding compound from Expt. 2 showed no melting point depression.

b) The picrate of the amine of structure $CH_3CCl = CBr-CH_2N(CH_3)_2$ was obtained, stereoisomeric to that described above, by reacting excess dimethylamine with 1,3-dichloro-2,3-dibromobutane, which in turn was obtained by brominating 1,3-dichlorobutene-2. Constants of $CH_3CClBr-CHBr-CH_2Cl$: b. p. 88° at 8 mm; $n^{20}D$ 1.5502, d^{20}_4 1.9910; MR found 45.59, calculated 45.94.

Found %: C 16.98, 16.90; H 2.03, 2.01; Cl 25.08; Br 55.76. $C_4H_6Br_2Cl_2$. Calculated %: C 16.52; H 2.12; Cl 24.89; Br 56.11.

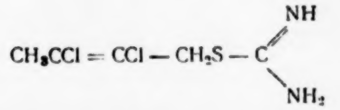
The amine obtained distilled at 58-60° at 4 mm, $n^{20}D$ 1.5030; m. p. of picrate 166-167° (from alcohol).

Found %: C 32.66, 32.68; H 3.11, 3.18; N 13.08, 13.07. $C_{12}H_{14}BrClN_4O_7$. Calculated %: C 32.63; H 3.19; N 12.68.

Reaction of HBr with $CH_3CCl_2Br = CH_2$ in the presence of benzoyl peroxide. A solution of 36.5 g of 2-bromo-3,3 -dichlorobutene-1 and 0.5 g of benzoyl peroxide in 112 g of carbon tetrachloride was saturated with hydrogen bromide for 30 min. The reaction product was washed with soda solution, water, and dried over $CaCl_2$. After evaporation of solvent and fractional distillation, 31.4 g (90% theoretical) of 1-bromo-2,3-dichlorobutene-2 (a mixture of cis-trans-isomers) was obtained with b. p. 64-70° at 15 mm; $n^{20}D$ 1.5310-1.5323, d^{20}_4 1.6519-1.6775; MR found 38.20-37.88, calculated 37.70.

Found %: C 23.60, 23.76; H 2.32, 2.42. $C_4H_5BrCl_2$. Calculated %: C 23.56; H 2.47.

By reacting with thiourea



was obtained, and isolated as the picrate with m. p. 197° (from alcohol).

Found %: N 16.56, 16.50; Cl 16.48, 16.33. $C_{11}H_{11}Cl_2N_5O_7S$. Calculated %: N 16.35; Cl 16.56.

On treatment of the mixture of 1-bromo-2,3-dichlorobutenes-2 with dimethylamine in alcohol, a good yield of a mixture of the stereoisomeric amines of structure $CH_3CCl = CCl-CH_2N(CH_3)_2$ was obtained, from which was isolated a fraction with b. p. 65-68° at 20 mm; $n^{20}D$ 1.4720; m. p. of picrate 144-145° (from alcohol).

Found %: C 36.25, 36.25; H 3.30, 3.37; N 14.39, 14.29 and a fraction with b. p. 75-77° at 20 mm, $n^{20}D$ 1.4750; m. p. of picrate 160-161° (from alcohol).

Found %: C 35.90, 35.89; H 3.68, 3.54; N 14.17, 14.19. $C_{12}H_{14}Cl_2N_4O_7$. Calculated %: C 36.28; H 3.55; N 14.11.

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INVESTIGATION OF THE AUTOOXIDATION OF ALKYL AND HALOGEN DERIVATIVES OF 1,1-DIPHENYLETHANE AND ISOPROPYLBENZENE

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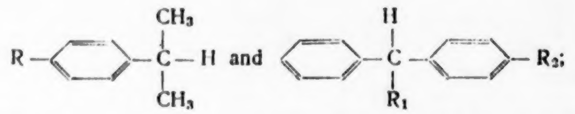
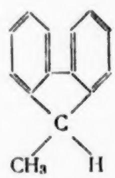
In previous works [1-5] it has been shown that on autooxidation of 1,1-diphenylethane and several of its alkyl derivatives the corresponding hydroperoxides are obtained. In the development of these works it was of interest to carry out an investigation of the preparation of the hydroperoxides of the halogen derivatives of aryl hydrocarbons, and also a more detailed study of the same autooxidation process of the initial aryl hydrocarbons and halogen derivatives in connection with their structure. The present work had as its aim the study of the influence of aryl and alkyl radicals, and also of halogens, on rate of autooxidation. For the investigation, compounds of the following structure were selected



where R = H, Cl, Br, I; $R_1 = CH_3, C_2H_5$, n-C_3H_7; R_2 = H, CH_3, C_2H_5, iso-C_3H_7, tert-C_4H_9, and also Cl, Br, I.

In addition, for comparison 9-methylfluorene was also investigated:



Compounds of the structure indicated were prepared by various methods. Isopropylbenzene was prepared from the technical product by careful purification. The following hydrocarbons were synthesized by well-known methods: 1,1-diphenylethane [1-3], 1,1-diphenylpropane [4], 1,1-diphenyl-n-butane [5], and the alkyl derivatives of 1,1-diphenylethane (methyl, ethyl, isopropyl, and tert-butyl) [5]. 9-Methylfluorene was prepared by organomagnesium synthesis from fluorenone and methyl iodide with subsequent reduction of the carbinol. Halogen derivatives of isopropylbenzene were prepared by the following methods. Parachloroisopropylbenzene – from chlorobenzene and isopropyl bromide with anhydrous aluminum chloride as catalyst. Parabromoisopropylbenzene – by direct bromination of isopropylbenzene [6]. Paraiodoisopropylbenzene from paranitroisopropylbenzene via the corresponding diazo compound [7].

Halogen derivatives of 1,1-diphenylethane were prepared by condensing styrene with the corresponding halobenzenes by the method which was developed in the laboratory for 1,1-diphenylethane [2, 3]. However, yields of halogen derivatives of 1,1-diphenylethane proved to be somewhat smaller (50-55%) than yield of hydrocarbons.

The substances enumerated were purified in a suitable manner, since this is necessary for the autooxidation process.

We carried out the investigations on autooxidation in an alkaline medium under optimum conditions developed in our laboratory for 1,1-diphenylethane [2, 3], vis.: to the substance to be oxidized was added a 5% solution of

caustic soda at the rate 0.05% of pure caustic soda and 1% of water on weight of product used. To obviate an induction period, the hydroperoxide also of the substance to be oxidized was added in pure form or as a concentrate in amount 0.5% of sample weight. The experiments were conducted in small 50 ml reactors of usual chemical glass; air was introduced through a capillary tube (immersed in the substance to be oxidized) at the rate of 25-30 ml per minute. Thirty g samples were selected for the experiment. Autooxidation rate was determined iodometrically by amount of hydroperoxide formed. The experiments were conducted at 80, 90, and 100°.

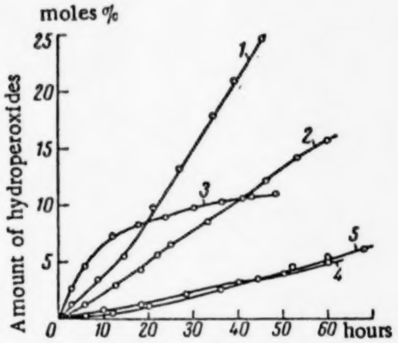


Fig. 1. Rate of hydroperoxide formation during autooxidation: 1) Isopropylbenzene; 2) 1,1-diphenylethane; 3) 9-methylfluorene; 4) 1,1-diphenylpropane; 5) 1,1-diphenyl-n-butane.

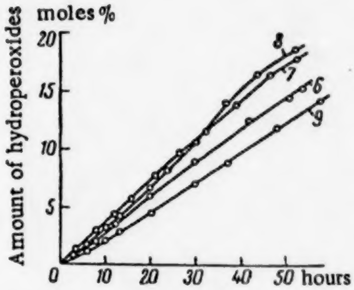


Fig. 2. Rate of hydroperoxide formation during autooxidation: 6) 1-Phenyl-1-p-tolylethane; 7) 1-phenyl-1-p-ethylphenylethane; 8) 1-phenyl-1-p-isopropylphenylethane; 9) 1-phenyl-1-p-tert-butylphenylethane.

From the results shown in Fig. 1 for 90° (curves 1, 2, and 3), it is seen that isopropylbenzene is oxidized more rapidly than 1,1-diphenylethane, but 9-methylfluorene, isomeric to the latter, is initially oxidized at a greater rate than both the foregoing hydrocarbons. Consequently, accumulation of phenyl residues at the tertiary C-atom retards autooxidation, this at first glance seeming rather confusing.

It is known [8] that phenyl radicals exert a positive influence on autooxidation, especially in the case of monoaryl hydrocarbons. It is obvious when two phenyl radicals are attached to a tertiary C-atom that, according to our ideas, retardation of autooxidation of 1,1-diphenylethane occurs because of the occurrence of steric hindrance in the free-radical autooxidation process. According to current ideas on this process in the case of a large volume, the peroxide radical $(C_6H_5)_2CH_3COO$, should react with the hydrogen of the tertiary C-atom of the initial hydrocarbon $(C_6H_5)_2CH_3C-H$, where the hydrogen is also to a large extent shielded by phenyl residues. As confirmation of these postulates there exists the data already known [9, 10], which shows that on autooxidation of triphenylmethane its hydroperoxide is not formed, but only triphenylmethyl peroxide. In the light of the proposition expressed regarding the role of steric hindrance, the data on acceleration of autooxidation of 9-methylfluorence becomes understandable because there, owing to the coupling of phenyl radicals and their orientation in the one plane, steric hindrance is less evident, but the positive influence of the phenyl residues on the autooxidation process is maintained. The only evidence of the specificity of 9-methylfluorene is the fact that in the autooxidation process extent of its conversion into hydroperoxide remains slight as a result of the low thermal stability of the hydroperoxide itself, which has been obtained by us in pure crystalline form and is at the present moment being studied in detail.

The results given in Fig. 1 (curves 4, 5) show that 1,1-diphenylpropane and 1,1-diphenyl-n-butane are oxidized to the corresponding hydroperoxides even more slowly than 1,1-diphenylethane. Retardation of autooxidation of these hydrocarbons is explained by us also by development of steric hindrance at the tertiary C-atom as a result of elongation of the aliphatic chain.

In Fig. 2 data is given on the autooxidation of paraalkyl derivatives of 1,1-diphenylethane at 90°, from which it is seen that 1-phenyl-1-p-tolyethane and 1-phenyl-1-p-tert-butylphenylethane (curves 6, 9) are oxidized at the same rate as 1,1-diphenylethane. However, somewhat more rapidly oxidized are 1-phenyl-1-p-ethylphenylethane and 1-phenyl-1-p-isopropylphenylethane (curves 7, 8), which fact is evidently connected with the partial oxidation of the alkyls mentioned into the corresponding hydroperoxides, as shown in the work of K. S. Grigor'eva [11]. Thus,

this data shows that radicals occurring in one of the benzene nuclei of 1,1-diphenylethane in the para-position do not affect to any great extent the autooxidation rate. These observations, in comparison with the foregoing, confirm that structural factors (presence of alkyl and aryl radicals) exert a particularly strong effect when they are altered at the tertiary C-atom, where, according to present thoughts [12], autooxidation occurs. Thus, according to our ideas, the influence of these structural factors is explained by steric hindrance.

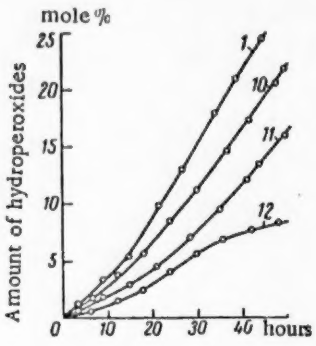


Fig. 3. Rate of hydroperoxide formation during autooxidation: 1) Isopropylbenzene; 10) p-chloroisopropylbenzene; 11) p-bromoisopropylbenzene; 12) p-iodoisopropylbenzene.

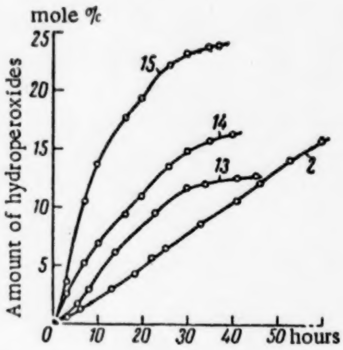


Fig. 4. Rate of hydroperoxide formation during autooxidation: 2) 1,1-Diphenylethane; 13) 1-phenyl-1-p-chlorophenylethane; 14) 1-phenyl-1-p-bromophenylethane; 15) 1-phenyl-1-p-iodophenylethane.

In Fig. 3 data is given on the autooxidation of para-halogen derivatives of isopropylbenzene at 90°, from which it is seen that halogens influence negatively the autooxidation process and with regards to their retarding effect can be arranged in the order: Cl < Br < I. In addition, from the data given in Fig. 4, it is seen that halogens in the para-position in one of the benzene nuclei of 1,1-diphenylethane have a positive effect on autooxidation, i.e., para-halogen derivatives of 1,1-diphenylethane are oxidized more rapidly to the corresponding hydroperoxide, and the halogens can be arranged in the reverse order I > Br > Cl with respect to their accelerating influence.

The difference observed in the effect of halogens in derivatives of monoaryl (isopropylbenzene) and diaryl (1,1-diphenylethane) hydrocarbons on the autooxidation process can be explained by the dual character of the halogens, with their participation on the one hand in electron migrations and, on the other, in linkage effects. In our case the order of the retarding effect of the halogens in isopropylbenzene is evidently explained by lowering of the activity of free radicals and of hydrogen mobility at the tertiary C-atom as a result of weakening of the polarizing effect of the halogens in the order Cl > Br > I. As is known, a similar order for the retarding effect of halogens is also observed in polymerization of halovinyls and para-halostyrenes.

The activating effect of halogens in halogen derivatives of 1,1-diphenylethane can probably be explained by the polarizability of halogens and by their participation in the linkage of double bonds. In our case, in the presence of two benzene nuclei, linkage of unsaturated bonds of the nucleus takes place through the tertiary C-atom, halogens in such a system exerting a positive effect in such an order that the greater the polarizability of the halogen, the greater is its positive influence on autooxidation. Similar regularity is observed in polymerization of 2-halo-substituted butadiene-1,3, in which occurs conjugation of a double bond system.

In addition to the results given above we obtained data on autooxidation of all the compounds enumerated at 80 and 100° and at the present moment are examining it analytically.

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STRUCTURE OF COMPLEX COMPOUNDS OF STANNIC CHLORIDE WITH ESTERS

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One of the basic problems in the study of the structure of the complex compounds of acids with esters is to determine which of the oxygen atoms of the ester participates in bond formation.

Baeyer and Villiger [1], Pfeiffer [2], and Chelintsev [3] assumed that in the oxonium compounds of esters bonding takes place at the carbonyl oxygen. Kurnakov et. al., [4] attributed this bonding to the oxygen of the alkoxyl group. According to J. Kendall [5], there is no sufficient evidence to solve the problem in favor of the one or the other of the oxygen atoms of an ester. Authors reporting optical studies on the intermolecular reactions of esters with acids [6-9] favor bonding at the carbonyl oxygen. At the same time, condensation of esters with aromatic compounds is known to lead not only to alkylation, but also to the acylation of the latter compounds. The mechanism of such an acylation can be understood easier, if one assumes that the addition of esters to condensing agents occurs at the oxygen of the alkoxyl group, as this reaction must be accompanied by a weakening of the bond between the alkoxyl oxygen and the acyl group.

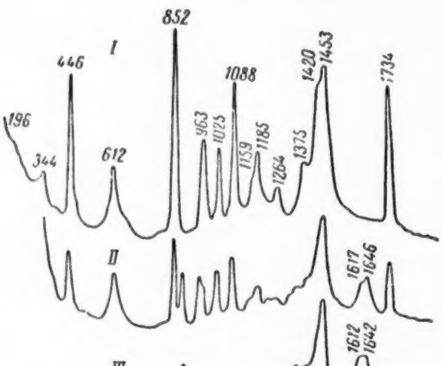


Fig. 1. Raman spectra of methyl propionate and its mixtures with stannic chloride. I) ester; II) mixture 20 mol % $SnCl_4$; III) 25 mol % $SnCl_4$; IV) 33.3 mol % $SnCl_4$; V) 50 mol % $SnCl_4$.

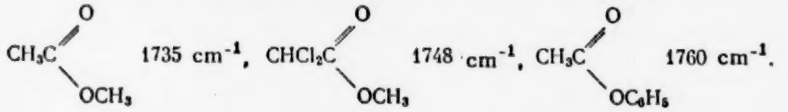
We carried out a comparison between the Raman spectra of 11 esters and those of their mixtures with stannic chloride in a wide concentration range.

As an example, we have given in Fig. 1-3, the spectra of some esters and their mixture with stannic chloride.

A consideration of Fig. 1 shows that as stannic chloride is added to methyl propionate, i.e., as we pass from spectrum I to spectrum V, the intensity of the frequency around 1730 cm^{-1} belonging to the vibration of the carbonyl group gradually diminishes (spectra II and III), and vanishes completely when the concentration of stannic chloride attains 33.3 mol %, which corresponds to the compound $SnCl_4 \cdot 2RCOOR'$ (spectrum IV). Instead of this frequency at 1730 cm^{-1}, there appears in solutions of stannic chloride in methyl propionate a new split frequency of 1610-1640 cm^{-1}, the intensity of which increases with an increase in stannic chloride concentration. Quite similar spectral changes are observed with solutions of stannic chloride in methyl formate (Fig. 2) and methyl acetate (Fig. 3).

If one takes into account the fact that the gradual disappearance of the 1730 cm^{-1} frequency (characterizing the vibration of the carbonyl group of free ester molecules) brought by increasing the concentration of stannic chloride accompanied by an increase in the intensity of the shifted frequency, one may conclude that the latter belongs to the vibration of the C=O group in the complex.

This allows us to assert that the addition of stannic chloride to an ester molecule occurs at the carbonyl oxygen. This deduction can be also confirmed by the following consideration. If stannic chloride added itself at the site of the alkoxyl oxygen, one would expect an increase in the frequency of the C=O group, as it is known that the introduction of acceptor atoms and groups in the molecule of an ester increases the frequency of the C=O group:



However, one observes (Fig. 1-3) a decrease in the frequency of the C=O group. This decrease is of the same order as the one displayed by the C=O group in acetone [10], the addition of which to stannic chloride at the site of the carbonyl group cannot be subjected to doubt.

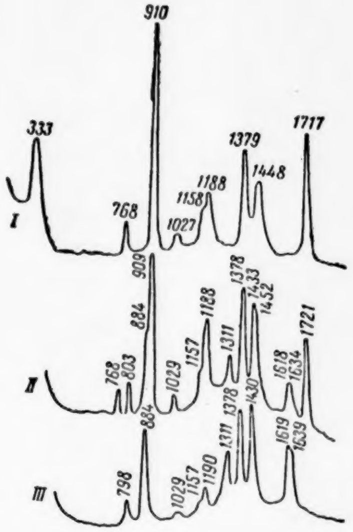


Fig. 2. Raman spectra of methyl formate and its mixtures with stannic chloride. I) ester; II) mixture 12% mol % $SnCl_4$; III) 50 mol % $SnCl_4$.

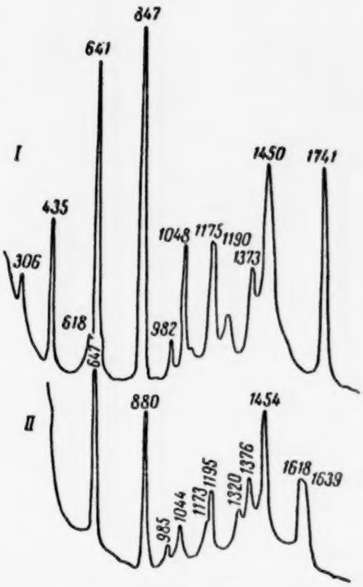
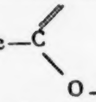
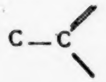


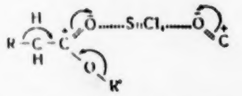
Fig. 3. Raman spectra of methyl acetate and its mixtures with stannic chloride. I) ester; II) 6.67 mol % $SnCl_4$.

Thus, the combination of these data allows us to conclude that esters add themselves to stannic chloride at the carbonyl oxygen. Bystrov and Filimonov [9] reached the same conclusion on the basis of their study of the infrared spectra of mixtures of esters with metal halides. By taking into consideration the fact that the addition of the C=O group to Sn^{4+} should lead to a change in the whole ester molecule because of the mutual influence of the atoms in the molecule upon one another, we thought that it would be interesting to follow, as far as possible, the changes occuring in the frequencies of all the bonds in the ester molecule.

Spectra of esters with stannic chloride display a new frequency in the region of 1320 cm^{-1}. Examination of the literature data [8, 11, 12] allows to attribute it preferably to the vibration of the , bond, shifted toward higher frequencies. In the case of methyl acetate (Fig. 3), this is illustrated by the considerable frequency displacement from 1252 cm^{-1} to 1320 cm^{-1}. The frequency increase in the range from 850 cm^{-1} to 880 cm^{-1} (Fig. 1 and 3), which is attributed [13] mainly to the vibration of the  bond siturated in the neighborhood of the

carbonyl group, is evidence for its strengthening. In the spectrum of methyl formate (Fig. 2), one observes the frequency decrease of the O-CH_3 bond [12, 14] from 910 cm^{-1} to 884 cm^{-1}. The observed change in the frequencies of bond vibrations in ester molecules under the influence of their addition to stannic chloride can be apparently explained by the electronic shifts along the bonds in the whole molecule [15].

These shifts in the Raman spectra allow to propose the structure of complex compounds of stannic chloride with esters which are illustrated by the following scheme:



Such a distribution of the electron cloud in the molecule must increase the possibility of the aliphatic radical of the alkoxyl group to be split as an alkyl cation R^+, i.e., it should lead to an increase in the acid character of the ester, and to its electrolytic dissociation. However, the alkyl cation is not capable to have a lasting independent existence in solution, and it splits off only in the presence of molecules to which it can add itself. Among such molecules capable of accepting an alkyl cation are the ester molecules themselves. For this reason, the electrolytic dissociation of complex compounds of the type $SnCl_4 \cdot 2RCOOR'$ with the separation of alkyl cations occurs in the presence of an excess of ester molecules, compounds of the type $SnCl_4 \cdot 3RCOOR'$ and $SnCl_4 \cdot 4RCOOR'$ being formed [16, 17].

Let us follow now the behavior of the new split frequency at 1610-1640 cm^{-1} of stannic chloride solutions in esters when the concentration of stannic chloride is changed. It clearly appears in Fig. 1 that the intensity of the high frequency component of the 1640 cm^{-1} band increases with an increase in the concentration of the ester (change from spectrum V to spectrum II) when conditions become favorable for the formation of compounds of type $SnCl_4 \cdot 3RCOOR'$ and $SnCl_4 \cdot 4RCOOR'$, and, on the contrary, tends to vanish with an increase in the concentration of stannic chloride (change from spectrum II to spectrum V). On the other hand, when the concentration of stannic chloride is increased, i.e., in the concentration region where compound $SnCl_4 \cdot 2RCOOR'$ prevails, one observes an increase of intensity of the band component around 1610 cm^{-1} (change from spectrum II to spectrum V).

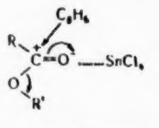
Such a behavior of the split band accompanying concentration changes of the solutions naturally suggests that the frequency around 1610 cm^{-1} should be attributed to the vibration of the C=O group in the complex compound $SnCl_4 \cdot 2RCOOR'$, and the frequency around 1640 cm^{-1} to the vibration of the carbonyl group in anions

$$SnCl_4 \begin{matrix} RCOO^- \\ RCOOR' \end{matrix} \quad \text{or} \quad SnCl_4\,(RCOO)_2^{2-}.$$

The possibility of a dissociation of the alkyl cation R^+ in the complex compound and of its reaction with aromatic hydrocarbons suggests an ionic mechanism for the alkylation of the latter compounds:

$$SnCl_4\,(RCOOR')_2 + C_6H_6 = SnCl_4 \begin{matrix} RCOO^- \\ RCOOR' \end{matrix} + C_6H_6R'^{+} = SnCl_4 \begin{matrix} RCOOH \\ RCOOR' \end{matrix} + C_6H_5R\,.$$

On the other hand, the proposed structure of the complex compound allows to assume that the acylation reaction of aromatic compounds by esters in the presence of stannic chloride proceeds through the formation of ternary complexes:



Thanks to the reaction of the acylating agent (an electron donor) with the positive carbon atom, the dynamic electron shift and the dissociation of the −C−OR' bond become possible.

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INTERSECTION OF THE STABLE AND NONEQUILIBRIUM TETRAHEDRA IN THE SEPTERNARY RECIPROCAL SYSTEM Li, Na, Rb, Tl ‖ Br, Cl, NO_3, SO_4

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(Presented by Academician I. V. Tananaev, November 16, 1960)
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Original article submitted November 14, 1960

Exchange reactions in reciprocal systems are reflected on the composition diagram by intersection of the nonequilibrium elements with stable intersection elements [1].

The composition diagram of a septernary reciprocal system of 16 salts is a six-dimensional polytope [2]. In the singular star of the system Li, Na, Rb, Tl ‖ Br, Cl, NO_3, SO_4, in the center of the cube which orients the star, there is a basic tetrahedron $LiSO_4-NaCl-RbNO_3-TlBr$, which is the most stable tetrahedron. The nonequilibrium tetrahedron of this system reflects the most reactive salts, which, by reacting among themselves, form the components of the system represented by the stable tetrahedron. Both tetrahedra lie in the six-dimensional space of the composition diagram of the septernary system and intersect along the conversion line. The exchange reactions in the septernary reciprocal system Li, Na, Rb, Tl ‖ Br, Cl, NO_3, SO_4 can be represented by equations for the nonequilibrium tetrahedron:

$$RbCl + NaNO_3 = RbNO_3 + NaCl \qquad RbCl + LiBr = RbBr + LiCl$$

$$LiBr + \frac{1}{2} Tl_2SO_4 = \frac{1}{2} Li_2SO_4 + TlBr \quad LiBr + NaNO_3 = LiNO_3 + NaBr$$

$$RbCl + \frac{1}{2} Ti_2SO_4 = \frac{1}{2} Rb_2SO_4 + TlCl \quad NaNO_3 + \frac{1}{2} Tl_2SO_4 = \frac{1}{2} Na_2SO_4 + TlNO_3$$

and for the equilibrium tetrahedron:

$$NaNO_3 + RbCl = NaCl + RbNO_3 \qquad LiNO_3 + \frac{1}{2} Rb_2SO_4 = \frac{1}{2} Li_2NO_4 + RbNO_3$$

$$LiBr + \frac{1}{2} Tl_2SO_4 = \frac{1}{2} Li_2SO_4 + TlBr \qquad LiCl + \frac{1}{2} Na_2SO_4 = \frac{1}{2} Li_2SO_4 + NaCl$$

$$TlNO_3 + RbBr = TlBr + RbNO_3 \qquad NaBr + TlCl = NaCl + TlBr$$

Summing all equations and dividing by four, we obtain the equation for the exchange reaction:

$$LiBr + NaNO_3 + RbCl + \frac{1}{2} Tl_2SO_4 = \frac{1}{2} Li_2SO_4 + NaCl + RbNO_3 + TlBr.$$

In addition to the exchange reaction, complex formation takes place in the system, and this results in the appearance of a series of binary complex salts: $Li_2SO_4 \cdot Rb_2SO_4$, $4Li_2SO_4 \cdot Rb_2SO_4$, $RbCl \cdot 2Li_2SO_4$ and, possibly, others.

The stable tetrahedron of the system has been investigated experimentally [4]. It therefore appeared to be of considerable interest to carry out an experimental study of the line of intersection of the stable and nonequilibrium tetrahedra starting with the components of the two tetrahedra. Figure 1 shows the melting diagram; the circles represent data obtained by the visual-polythermal method with the salts of the stable tetrahedron (0.5 NaCl + $0.5RbNO_3$) – $\left(0.5 \frac{Li_2SO_4}{2} + 0.5\ TlBr\right)$, and the crosses represent similar data of the nonequilibrium tetrahedron (0.5 $NaNO_3$ +

+ 0.5 RbCl) – $\left(0.5\ LiBr + 0.5\ \frac{Tl_2SO_4}{2}\right)$. The liquidus line consists of two crystallization branches: NaCl and Li_2SO_4. The Li_2SO_4 curve has a separation region which begins at the 35 mole % mixture $\left(0.5\ \frac{Li_2SO_4}{2} + 0.5\ TlBr\right)$ or $\left(0.5\ LiBr + 0.5\ \frac{Tl_2SO_4}{2}\right)$ and extends to 100%. On the lithium sulfate crystallization branch under the separation region there is a smooth break, after which the melting points of the mixture begin to increase rapidly. However, it was not possible to investigate this region in more detail owing to decomposition of the nitrates and sublimation of the thallium salts at temperatures above 500°. We did record thermograms of mixtures corresponding to compositions of the central points of the intersection line (Fig. 2); these mixtures were prepared from the salts corresponding to the apexes of the stable and the nonequilibrium tetrahedra. The table presents the temperatures of the plateaus and the corresponding phases.

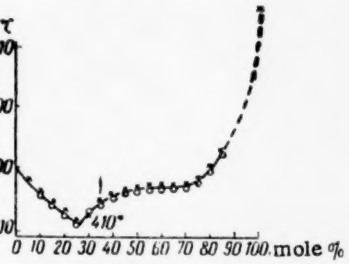

Fig. 1. Melting diagram for the conversion line, the intersection of the two tetrahedra.

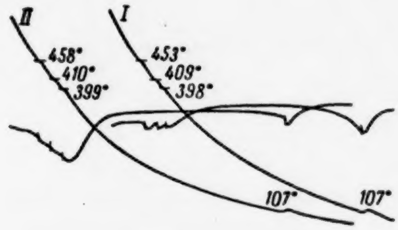

Fig. 2. Cooling curves for the central points of the conversion line along the intersection of the stable and nonequilibrium tetrahedra.

Tetrahedron	Plateau 1		Plateau 2		Plateau 3		Plateau 4	
	temp. °C	phase	temp. °C	phase	temp. °C	phase	temp. °C	phase
Stable	453	Li_2SO_4	409	Li_2SO_4 NaCl	398	Li_2SO_4 TlBr NaCl	107	Li_2SO_4 TlBr NaCl $RbNO_3$
Nonequilibrium	458	Li_2SO_4	410	Li_2SO_4 NaCl	399		107	

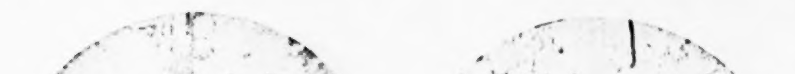

Fig. 3. Microstructures of the mixtures corresponding to the central point of the line of intersection of the stable (a) and nonequilibrium (b) tetrahedra.

The thermograms are identical, as an examination of the table reveals. There are four plateaus on the cooling curves of the mixtures: the first plateau, at 453°, corresponds to the separation of the first crystals of Li_2SO_4; the second, at 409°, corresponds to the simultaneous separation of Li_2SO_4 and NaCl; the third plateau, at 391°, corresponds to the simultaneous separation of Li_2SO_4, NaCl, and TlBr; and, finally, at 107° there is a significant effect corresponding to a quaternary eutectic, at which point $RbNO_3$ has been added to the first three phases.

Figures 3a and 3b show the microstructures of mixtures having compositions corresponding to the central points of the stable and nonequilibrium tetrahedra. The microstructures of these two mixtures are equivalent.

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THE SYSTEM COMPOSED OF SODIUM AND COPPER ARSENATES AND CARBONATES

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Original article submitted December 14, 1960

In our earlier papers [1, 2] we published data obtained in an investigation of the aqueous system of copper and sodium arsenates and sulfates. It was found that the hydrated binary compound copper arsenate sulfate is formed during interaction of these salts. The existence of this double salt impelled us to determine the behavior of copper arsenate with sodium and potassium nitrates, chlorides, and carbonates.

The present work was devoted to a study of the system composed of copper arsenate, sodium carbonate and water. Chemically pure copper arsenate was prepared for use in this work. The sodium carbonate was purified by recrystallization.

The study was carried out by the well-known isothermal method at 50° in a water bath; the temperature of the water was maintained within ±0.1°. The system formed by copper arsenate and sodium carbonate in water is a (quaternary), reciprocal system. However, since copper arsenate and carbonate are difficultly soluble in water while the corresponding sodium salts are highly soluble, the system can provisionally be considered as the simple ternary system copper arsenate—sodium carbonate—water.

Equilibrium between the liquid and solid phases is established relatively slowly in this system; consequently, the samples were held in the bath for from two to ten days and for twice as long in the case of transition points. The mixtures were formed in the reaction vessel by first charging the copper arsenate (about 10-15 g) and sodium carbonate (2 g) and then adding the water. Then, as the investigation proceeded, 1-2 g of sodium carbonate was added each time a sample was taken. Establishment of equilibrium was determined by chemical analysis; equilibrium was considered to be established when two successive analyses gave the same or almost the same result for arsenate ion in the solution. Homogeniety of the solid phases was checked by microscopic examination. Samples of the solution and of the solid phase in equilibrium with the solution were taken simultaneously.

The contents of arsenate, carbonate, and copper ions were determined in the liquid and solid phases. Arsenate ion was determined by the iodometric method of Shakhtakhtinskii [3]. Carbonate ion was determined by the well-known calcium method. The copper ion content was determined gravimetrically as copper oxide (CuO). The sodium was determined by difference.

The data resulting from the investigation of the solubility relationships in the system copper arsenate—sodium carbonate—water are presented in the table. The solubility of copper arsenate was low; it comprised only 0.001%.

The sodium carbonate solubility was 32.16%. The limiting concentration of pure sodium arsenate at this temperature is 49.06% [2]. As may be seen from the table, when the sodium carbonate concentration was increased to 7.08%, the amount of copper and sodium arsenates in the solution increased to 19.82%. These solutions were in equilibrium with the copper arsenate precipitate.

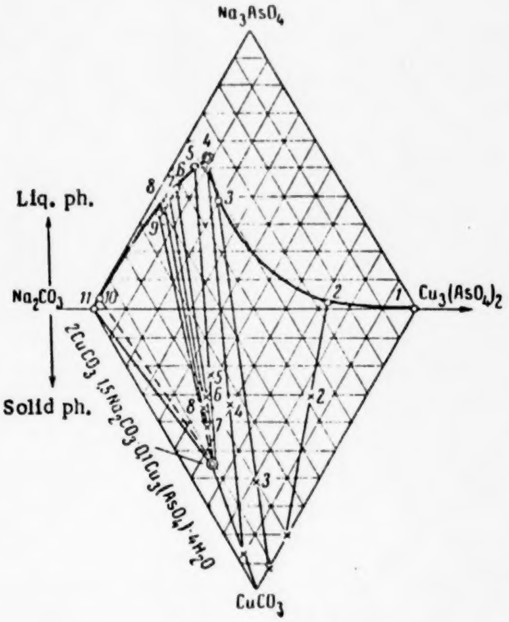
With the aim of more graphically representing the nature of the changes in the equilibrium state of the system, we constructed the solubility diagram (figure). The diagram consists of two isosceles triangles joined at their bases along the sodium carbonate—copper arsenate line. The general form of the diagram is that of a rhombus. Data on the solubilities of the salts were plotted in the upper triangle. Sodium arsenate, copper arsenate, and sodium carbonate, were plotted at the corners of the upper triangle. Copper carbonate is not present in the upper triangle, since this salt is practically insoluble in water. The compositions of the solid phases are represented in the lower triangle. Copper arsenate, sodium carbonate, and copper carbonate are plotted at the corners of the lower triangle.

Chemical Compositions of Solutions and Solid Phases in the System $Cu_3(AsO_4)_2-Na_2CO_3-H_2O$ at 50°

Expt. No.	Liquid phase									Solid phase									Solid phase
	In wt. percent						In percent of total salt			In wt. percent					In percent of total salt				
	Na_2CO_3	$Cu_3(AsO_4)_2$	Na_3AsO_4	$CuCO_3$	total salt	H_2O	Na_2CO_3	$Cu_3(AsO_4)_2$	Na_3AsO_4	Na_2CO_3	$Cu_3(AsO_4)_2$	Na_3AsO_4	$CuCO_3$	total salt	Na_2CO_3	$Cu_3(AsO_4)_2$	Na_3AsO_4	$CuCO_3$	
1	—	0,001	—	—	0,001	99,999	—	100	—	—	—	—	—	—	—	100	—	—	$Cu_3(AsO_4)_2 \cdot 4HO$
2	7,08	19,70	0,12	—	26,90	73,10	26,32	73,23	0,45	12,23	38,21	—	21,87	72,31	16,90	52,84	—	30,25	$Cu_3(AsO_4)_2 \cdot 4H_2O + CuCO_3$ (?)
3	13,05	5,31	10,75	—	29,11	70,89	44,83	18,24	36,93	9,33	8,79	—	31,75	49,87	18,71	17,63	—	63,66	$Cu_3(AsO_4)_2 \cdot 4H_2O + CuCO_3$ (?)
4	11,25	2,78	16,22	—	30,25	69,75	37,19	9,19	53,62	29,73	18,72	—	25,41	73,86	40,25	25,34	—	34,41	$CuCO_3$(?) + $0,1Cu_3(AsO_4)_2 \cdot 2CuCO_3 \cdot 1,5Na_2CO_3 \cdot 4H_2O$
5	15,58	1,60	18,47	—	35,65	64,35	43,70	4,49	51,81	38,22	18,03	—	16,59	72,84	52,47	24,75	—	22,78	$0,1Cu_3(AsO_4)_2 \cdot 2CuCO_3 \cdot 1,5Na_2CO_3 \cdot 4H_2O$
6	16,02	1,74	12,71	—	30,47	69,53	52,58	5,71	41,71	35,06	12,11	—	22,85	70,02	50,07	17,30	—	32,63	$0,1Cu_3(AsO_4)_2 \cdot 2CuCO_3 \cdot 1,5Na_2CO_3 \cdot 4H_2O$
7	18,42	1,20	14,79	—	34,41	65,59	53,53	3,49	42,98	27,31	7,50	—	23,82	58,63	46,58	12,78	—	40,64	$0,1Cu_3(AsO_4)_2 \cdot 2CuCO_3 \cdot 1,5Na_2CO_3 \cdot 4N_2O$
8	14,46	0,98	10,16	—	26,10	73,90	57,32	3,75	38,93	32,82	12,83	—	25,18	70,83	46,34	18,11	—	35,55	$0,1Cu_3(AsO_4)_2 \cdot 2CuCO_3 \cdot 1,5Na_2CO_3\ 4H_2O$
9	16,98	1,52	9,41	—	27,91	72,09	60,84	5,45	33,71	38,14	12,90	—	26,91	77,95	48,93	16,55	—	34,52	$0,1Cu_3(AsO_4)_2 \cdot ?CuCO_3 \cdot 1,5NaCO_3 \cdot 4H_2O$
10	29,85	—	2,29	—	32,14	67,86	92,87	—	7,13	42,76	9,98	—	25,53	78,27	54,63	12,75	—	32,62	$0,1Cu_3(AsO_4)_2 \cdot 2CuCO \cdot 1,5Na_2CO_3 \cdot 4H_2O$
11	32,16	—	—	—	32,16	67,84	100	—	—	—	—	—	—	—	100	—	—	—	$Na_2CO_3 \cdot H_2O$

As a consequence of the fact that sodium arsenate is highly soluble and does not precipitate in the solid phase, there is no point corresponding to it in the solid phase composition triangle. The numbered points representing equilibrium solutions and solid phases were plotted on the composition triangle by the method proposed by Roozeboom. For this purpose, the concentrations of salts in solution and in the solid phase were recalculated to percent of total salt. This type of diagram is new, and this is the first time such a diagram has been constructed. It seems to us that this type of diagram is quite convenient for characterizing reciprocal systems in which the components have sharply differing solubilities and in which one or two salts of reciprocal pairs are almost insoluble.

Solubility diagrams constructed on this principle are characterized by curves consisting of two branches. The first branch, from points 1 to 4, corresponds to crystallization of copper arsenate tetrahydrate in the solid phase. The degree of hydration of the copper arsenate was established by chemical analysis. Water is not shown on the diagram as a component part of any solid phase. The copper and sodium arsenate concentration in the solutions varied from 0.001 to 19.82%. The total arsenate content at transition point 4 was 19.00%. The straight lines connecting numbered points of solutions and precipitates indicate the presence of a mixture of copper arsenate and carbonate in the solid phases. The solubility branch in this interval of concentration is represented by a curve convex to the copper arsenate—sodium carbonate side. Point 4 is a transition point, and is characterized by being the point farthest removed from the base toward the sodium arsenate corner.



Solubility diagram for sodium and copper arsenates and carbonates at 50°.

The solution at the transition point had the following composition: copper arsenate, 2.78%; sodium carbonate, 11.25%; sodium arsenate, 16.22%; and water, 69.75%. The second branch of the solubility curve, which proceeds from point 4 to point 10, corresponds to the crystallization of a triple salt containing sodium and copper carbonates and copper arsenate.

This new salt separated as well-formed crystals having the clearly expressed habit of hexagonal syngony. Under the microscope, the crystals appeared as cubic plates or low bipyramids. According to the solubility diagram, the new salt is characterized by the following contents of the basic components: copper carbonate, 47.07%; sodium carbonate, 30.28%; copper arsenate, 8.92%; water, 13.73%. These theoretical values for the composition of the triple salt were repeatedly confirmed by chemical analysis. The following composition of the salt was found by analysis: copper carbonate, 47.42%; sodium carbonate, 29.46%; copper arsenate, 8.72%; water, 14.40%. These values are in close agreement with the theoretical values.

The molar ratios of the basic components of this salt were calculated using the experimental data. This yielded the following chemical composition for the salt: $20CuCO_3 \cdot 15Na_2CO_3 \cdot Cu_3(AsO_4)_2 \cdot 40H_2O$.

In order to express more conveniently the composition of the salt, the coefficients of the components were divided by ten; this gives the following formula: $0.1\ Cu_3(AsO_4)_2 \cdot 2CuCO_3 \cdot 1.5\ Na_2CO_3 \cdot 4H_2O$. The composition plotted on the physicochemical diagram is for the anhydrous salt: copper arsenate, 10.34%; sodium carbonate, 35.11%; copper carbonate, 54.55% (figure).

The straight lines connecting the numbered points for solutions (from 5 to 10) and solid phase intersect at a single point on the diagram. That the straight lines so intersect suggests that a new solid phase in the form of a triple salt of constant composition was formed in the system. The sodium carbonate branch [from 10 to 11] is almost completely absent from the diagram in view of the formation of the difficultly soluble triple salt. This new hydrated triple salt, which was discovered in the present work and which is composed of copper arsenate, copper carbonate, and sodium carbonate, may find practical use. At our suggestion, this new salt has been tested at the Kirgiz Scientific

Research Institute of Animal Husbandry as a medicinal for domestic animals. N. E. Shkodin and D. K. Teslennikov have established that the preparation is an effective agent for the treatment of sheep infested with tape worms of the genus Moniezia.

Testing of the triple salt as a medicinal preparation is being continued.

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SYNTHESIS OF POLYMERIZING ANTIMONY ORGANIC ACRYLATES AND METHACRYLATES

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Derivatives of acrylic and methacrylic acids containing mercury [1], lead [1, 2], tin [3-5], and germanium [6] atoms have recently been synthesized. While continuing these studies, we synthesized antimony organic derivatives of acrylic and methacrylic acids for the first time.

Diphenylstibine acrylate $CH_2 = CHCOOSb(C_6H_5)_2$ and diphenylstibine methacrylate $CH_2 = C(CH_3)COOSb(C_6H_5)_2$ have been prepared.

The synthesis of unsaturated antimony organic compounds is carried out by the reaction of diphenylstibine oxide with acrylic (or methacrylic) acid in methanol solution, according to the scheme:

$$((C_6H_5)_2Sb)_2O + 2CH_2 = CR - COOH \rightarrow 2CH_2 = CRCOOSb\,(C_6H_5)_2 + H_2O,$$
$$R = H,\ CH_3$$

These substances are colorless crystalline compounds soluble in organic solvents. They polymerize easily, as such, or in solution, and also form copolymers with various vinyl monomers.

EXPERIMENTAL*

Diphenylchlorostibine was prepared by the reaction of tetraphenyl tin with antimony trichloride; it was further converted into the corresponding acetate, which was used to synthesize diphenylstibine oxide, m. p. 78° [7].

Diphenylstibine acrylate was prepared as follows: A solution of diphenylstibine oxide (5.7 g, 0.01 mole) in 50 ml of methanol, heated to boiling, was treated with a solution of acrylic acid (2.1 g, 0.03 mole) in 15 ml of methanol; the reaction mixture was then heated on a water-bath for 1 hr. The residue left after the removal of methanol was treated with n-hexane; upon cooling, the solution gave a crystalline precipitate. After a double recrystallization from n-hexane, colorless crystals, m. p. 115-117° were obtained. Yield, 5.1 g (74% of theoretical).

Found %: C 51.80, 52.12; H 4.24, 4.26; Sb 35.00, 35.43. $C_{15}H_{13}O_2$. Calculated %: C 51.87; H 3.74; Sb 35.15.

Diphenylstibine methacrylate was similarly obtained from diphenylstibine oxide (5.7 g, 0.01 mole), and methacrylic acid (2.6 g, 0.03 mole). The colorless crystals obtained after a double recrystallization from n-hexane weighed 5.5 g and melted at 113-115°.

Found %: C 53.47, 53.14; H 4.81, 4.75; Sb 33.80, 33.57. $C_{16}H_{15}O_2$. Calculated %: C 53.18; H 4.15; Sb 33.79.

Diphenylstibine acrylate and methacrylate have an irritant action on the higher respiratory tract, and provoke sneezing.

The monomers obtained polymerize easily as such, or in toluene solution when heated in the presence of azoisobutyric acid dinitrile (acting as initiator).

The polymers thus prepared are insoluble in organic solvents, and have a high sintering temperature. They readily copolymerize with methyl methacrylate and styrene, forming solid colorless thermoplastic products.

* With the participation of S. V. Troitskii.

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SYNTHESIS AND SOME OPTICO-MAGNETIC PROPERTIES OF POLYFERROCENES

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In the course of the present work on the investigation of the magnetic properties of various types of ferrocene derivatives, viz., polyferrocenylenes, polydiisopropylferrocene, polymethano- and polyethanopolyferrocenes, the unusual magnetic properies of these compounds were discovered. Each of these types of ferrocene derivatives was synthesized in the following manner:

A) Polyrecombination reaction [1, 2]. One mole of ferrocene (or, correspondingly, its diisopropyl homolog) was treated with 1-2 moles of tert-butyl peroxide at 200° in a nitrogen atmosphere. The formation of polyferrocenylene (and, correspondingly, of polyisopropylferrocene) can be represented in the following way: the tertiary butyl and methyl radicals formed during the dissociation of the peroxide remove a hydrogen atom from ferrocene (or an α-hydrogen of the isopropyl substituent of ferrocene); the radicals thus obtained recombine with the formation of linear polyferrocenylene (and, eventually, of polydiisopropylferrocene). Together with the linear benzene-soluble polyferrocene, an insoluble polymer (samples Nos. 5-6), apparently with a two- or three-dimensional structure, is obtained. The two polymeric forms of ferrocene were separated by treating the reaction product with benzene. The linear polymer was isolated from the benzene solution by a double reprecipitation with methanol. The filtrate was freed from benzene and methanol by distillation, and there remained a mixture of unreacted ferrocene and low-molecular compounds, from which ferrocene was separated by vacuum distillation. The conversion of ferrocene into high-molecular compounds attained 25%. The composition and structure of these products were confirmed by elementary analysis and infrared spectra which display absorption bands in the 1000-1100 cm^{-1} region, characteristic for a free cyclopentadiene ring. The polymers obtained appear as dark-red powders, and samples of polydiidopropylferrocene, as pale-yellow powders. Soluble polyferrocenylenes (samples Nos. 1-4) have a molecular weight of 370 to 7000, and a softening temperature of 290-300°. The molecular weight of samples Nos. 1-3 was determined cryoscopically, and of samples Nos. 4 ,7, ebullioscopically (in benzene, in both cases). The insoluble polyferrocene (Nos. 5,6) softens at 400°, this seems to indicate the presence of relatively few cross-linkages between linear chains.

B) Polyalkylenation of ferrocene with methylene chloride and 1,2-dichloroethane in the presence of aluminum chloride. Twenty grams of anhydrous aluminium chloride in 50 ml of dry dihaloalkane was gradually added to 40 g of ferrocene in 250 ml of the same solvent. The mixture was kept at the boiling point of the solvent for 6 hr with continuous stirring. On the next day, 10 g of anhydrous aluminium chloride in 25 ml of the same dihaloalkane was added to the reaction mixture. Heating at the boiling point of the solvent was continued with continuous stirring for a further period of 6 hr. Then, the reaction mixture was decomposed with ice and 10% hydrochloric acid. After treatment with sodium sulfite, the dihaloalkane solution was separated, and the aqueous solution was extracted with ether and benzene. The combined organic phase and extracts were washed with a 5% sodium carbonate solution followed by water, and were finally dried over fused calcium chloride. After removal of the solvents, the dry residue was extracted with methyl alcohol in a Soxhlet apparatus until the extracts became colorless. Ferrocene was recovered from this solution. The residue in the Soxhlet thimble contained the polyalkaneferrocenes, which have

different solubilities in ether and benzene. The molecular weight (cryoscopic method, in benzene) of the polymers obtained are given in the table. All the products readily soluble in benzene, had a decomposition temperature of about 115-120°. Product No. 9 was purified by reprecipitation with methanol from its ethereal solution. The yield of the pale yellow powder obtained was 9.5% with respect to ferrocene which participated in the reaction. Polymer No. 10 was reprecipitated from its solution in benzene by addition of n-heptane; the yield was 2%, the product appeared as a pale yellow powder. Polymer No. 11 was reprecipitated from its benzene solution with methanol; the yield of the grey-brownish product was 2.65%. All the powders were amorphous.

Polyferrocenylenes and polyalkanopolyferrocenes

No.	Substance	Mol. wt.	g-factor	Line width		N number		EPR signal in solution
				at 300°K	at 78°K	per g	per ring	
1	Linear polyferrocenylene	370		No signal				
2	" "	1000	2.00	150	300	$9.8 \cdot 10^{21}$	3	No
3	" "	2500	2.00	120	300	$8.9 \cdot 10^{21}$	2.7	Yes
4	" "	7000	2.00	120		$1.9 \cdot 10^{21}$	0.6	Yes
5	Insoluble polyferrocenylene		2.00	160	530	$3.9 \cdot 10^{22}$	12.3	
6	" "		2.00	150	460	$4.5 \cdot 10^{21}$	1.4	
7	Linear polydiisopropylferrocene	8000	–	–	No signal			–
8	Insoluble polydiisopropylferrocene		–	–	No signal			–
9	Condensation products of ferrocene with 1,2-dichloroethane	500	–	–	No signal			–
10	" "	2300	2.00	6.4	7.5	$5.4 \cdot 10^{17}$	$0.2 \cdot 10^{-3}$	No
11	" "	1000	2.00	6.4	7.5	$1 \cdot 10^{18}$	$0.4 \cdot 10^{-3}$	No
12	Condensation products of ferrocene with methylene dichloride	1000	–	–	No signal			
13	" "	2000	2.00	6.4	7.5	$5.6 \cdot 10^{18}$	$1.7 \cdot 10^{-3}$	Yes
14	Ferricinium cation	186	2.00	420	600			Yes

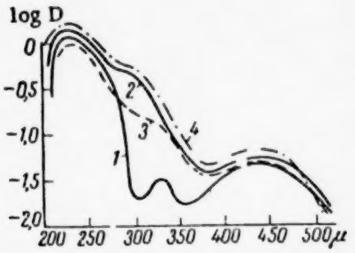
From the point of view of analytical results, substances Nos. 10 and 11 are related to pentaethanodiferrocene No. 9 [3], and it is possible that they consist of two or four molecules similar to this product, and bound by ethane bridges. The structure of substances Nos. 12 and 13 is under study. According to the analytical data, for each two ferrocene residues in the molecule of products No. 12 and 13, there are 4-5 methylene residues. All these substances are halogen-free. The infrared spectra of compounds Nos. 9-13 have frequencies in the 1000-1100 cm^{-1} range.

The study of the EPR spectra shows that polyferrocenylenes possessing π-conjugation between the ferrocene rings, as well as polyaromatic hydrocarbons [5] give an EPR signal (cf. the table).*

From the table it appears that an EPR signal is also given by polymers in which the ferrocene rings are separated by a $-CH_2-CH_2$-group [4]. In this connection, it is interesting to note that it was found during a study of the dibenzil anion [6] that the $-CH_2-CH_2$-group does not hinder the delocalization of an unpaired electron between the two phenyl rings. In the compounds presently described, and which give a EPR signal, the signal decreases with the decrease in the number of ferrocene rings. In polydiisopropylferrocenes this signal vanishes completely within the sensitivity limits of the measurements.

* The occurence of an EPR signal in the systems under investigation cannot be explained by the presence of a corresponding amount of the oxidized form of ferricinium cation. This follows from the method of synthesis (oxidized products are insoluble in ether and benzene), as well as from a comparison of the data obtained (cf. the table) with the results of the study of EPR spectra of ferricinium cation.

Polymers with low molecular weights do not give an EPR signal in benzene solution, but give it in the solid state. This result can be explained here, as well as in the case of polyaromatic hydrocarbons [5] by the fact that in the solid state intermolecular reactions lead to the occurence of conjugation between neighboring polymer molecules, and this, in turn, leads to the appearance of an EPR signal.



Absorption spectra of n-octane solutions of: 1) ferrocene; 2) polyferrocenylene with m.wt. 1000; 3) polydiisopropylferrocene; 4) absorption spectrum of ferrocene in CCl_4 [7].

All the polymers with which this signal has been observed give a single symmetrical EPR line of the Lorentz shape. The polyferrocenylene which is obtained by the polyrecombination method gives a wide EPR line (120 to 160 oe), the width of the line depending on the structure of the polymer. As the temperature is lowered, the line becomes wider; the width of the line being subjected to the greatest change in the case of low-molecular polymers. Polyalkaneferrocenes give a comparatively narrow EPR line (6.4 oe wide), the width of which depends only weakly upon the temperature. The g-factor of all the substances described which gave an EPR signal is the same and is equal to 2.00.

The determination of the concentration of unpaired electrons is usually carried out by comparison with the signal obtained with a standard, for the production of which one uses diluted paramagnetic substances. However, in the case under consideration, the nature of the signal is unclear, and we cannot assume that the numbers of unpaired electrons obtained by the given method correspond to their actual number. Nevertheless, the measured numbers can be used for characterizing the magnetic properties of the system. It appears from the table that in the case of different polyferrocenylene fractions with different molecular weights (cf. Nos. 2, 3 and 4), the "number of unpaired electrons" (N) per ring is different. In insoluble polyferrocenylene (cf. No. 5), the "number of unpaired electrons" per ring attains an abnormally high value. Apparently, this phenomenon is related to some collective effect of the ferromagnetic type.

During a study of ultraviolet spectra of polyferrocenylenes in n-octane solution, it was discovered that the spectra of polyferrocenylenes giving EPR signals in the solid state, are different from those given by the polyferrocenylenes which do not have EPR signals in the solid state. In the case of polyferrocenylenes giving an EPR signal, the ultraviolet spectrum completely coincides with the ultraviolet spectrum of ferrocene dissolved in carbon tetrachloride, a solvent in which, as it has been already shown [7], there occurs a charge transfer with the formation of the ionic pair $Fer^+CCl_4^-$, while in the case of polyferrocenylenes without EPR signals, the ultraviolet spectrum resembles the spectrum of ferrocene taken in a neutral solvent (n-octane), i.e., under conditions where there is no charge transfer.

During a study of polynucleotides and polyaromatic hydrocarbons, L. A. Blyumenfeld, A. A. Berlin, and others [5] have recently discovered magnetic properties unusual for organic compounds. Further, it has been assumed [8] that the anomalous magnetic properties of some organic macromolecular structures of definite structure, given by their discoverers the name of "pseudoferromagnetism" are related to the formation of intramolecular (or intermolecular) complex compounds with a charge transfer between valently saturated component parts. The collective reaction between unpaired electrons thus produced leads to the appearance of anomalous magnetic properties. The above mentioned data concerning ultraviolet spectra can be considered, to a certain degree, as a confirmation of this assumption.

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DIPOLE MOMENTS OF IMIDAZOLE AND ITS DERIVATIVES

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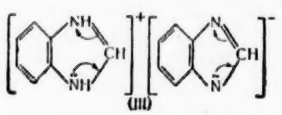
The classical structural formula of imidazole (I) does not account for the high dipole moments of its derivatives which vary according to different authors in the range of 3.6 to 6.2 D. Hückel, Datow, and Simmersbach [1] determined the dipole moments of 4-methylimidazole in nonpolar solvents, and gave them values between 6.2 and 4.8 D. These authors concluded that the constitution of imidazole corresponds to the structure of the bipolar ion (II), the positive center of which is concentrated on the immonium nitrogen, and the negative center, as a result of charge distribution around the ring in the center of the five-membered cycle. The calculated dipole moment of such a structure is 5.5 D, which is in acceptable concordance with experimental data.

However, the much lower value of the dipole moment of N-methylimidazole (3.6 to 3.8 D), Jensen and Friediger's data for the dipole moments of imidazole (3.84 D) and benzimidazole (3.98 D) [2], Syrkin and Shott-Lvova's data (4.08 D) [3], as well as calculations by the method of molecular orbitals [4] are in poor concordance with the amphionic structure of imidazole.

An original approach to the structure of benzimidazole derivatives in solution was proposed by L. S. Efros and B. A. Porai-Koshits [5] who assumed the possibility of formation of intermolecular ionic compounds (III):


(I)


(II)


(III)

In connection with the above mentioned facts, it was interesting to check the dipole moments as given by the different authors [1-3], and to discuss some questions pertaining to the fine chemical structure of imidazole and its derivatives.

In our experiments, we measured the dipole permeability of dioxane solutions by the method of resonance in conjunction with the replacement method, the experiments being carried out at 25° with concentrations of imidazoles from 0.002 to 0.02 M. The electronic polarization was calculated on the basis of the sum of bond refractions; the atomic polarization was not taken into account. The detailed method of determination has been described earlier [6].

The table contains dipole moment data of a number of imidazole derivatives, as well as those of N,N'-diphenylformamidine (IV).

Data of the table show that the magnitude of the dipole moment of the imidazole ring determines the values of the moments of its derivatives containing weakly polar substituents. At the same time, the character of carbocyclic rings condensed with the imidazole ring does not exert a considerable influence on the magnitude of the moment to which one may ascribe, on the basis of both our measurements and the data of other authors [2, 3], the value of about 4 D. This value characterizes the polarization of the imidazole ring as a whole and is not determined by the moment of the $-NH-CH=N-$ group; the value of 2.20 D obtained by us for the dipole moment of N,N'-diphenylformamidine (IV), which closely corresponds to the value calculated by the vector addition method, is a confirmation of this fact.

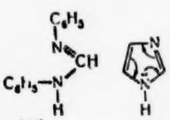
The observed values of the dipole moments of imidazole derivatives do not agree with the assumed complete ionization of the imidazole ring (II), and also contradict assumptions concerning the existence of an acid-base reaction leading to the formation of an intermolecular compound (III).

The dipole moments of compounds of type (III) have magnitudes of the order of 14-19 D [7]. Moreover, if such was really the structure of imidazole and benzimidazole derivatives, then one could expect wider differences between the moments of nonalkylated and alkylated compounds, as the latter, lacking a mobile hydrogen atom, are incapable of forming such salts. The results given in the table show that the dipole moments of alkylated and non-alkylated imidazole derivatives are almost the same.

No.	Substance	R_∞, ml	R_{el}, ml	μD
1	Imidazole	349.0	17.95	3.99
2	4,5-Diphenylimidazole	438.9	66.20	4.34
3	N-Ethyl-4,5-diphenylimidazole	427.0	75.69	4.11
4	Benzimidazole	374.2	34.74	4.03
5	N-Methylbenzimidazole	380.4	39.58	4.04
6	5,6,7,8-Tetrahydrobenzimidazole	354.8	34.48	3.98
7	Naphtho-(1,2)-imidazole	398.4	51.53	4.12
8	3-Methylnaphtho-(1,2)-imidazole	360.3	56.37	3.86
9	1-Ethylnaphtho-(1,2)-imidazole	394.4	61.02	4.04
10	N-Ethylphenanthreno-(9,10)-imidazole	424.0	77.81	4.11
11	5 (6)-Nitrobenzimidazole	765.1	40.43	5.95
12	N,N'-Diphenylformamidine	160.3	60.93	2.20

Thus, the magnitude of the dipole moments of imidazole derivatives cannot be explained either by the classical formula for the structure of imidazole (I), or by an intramolecular salt formula (II) and the intermolecular ionic structure (III). Abnormally high dipole moments of imidazole and 4-methylimidazole given by Hückel [1, 8] can be apparently explained by the fact that in the mentioned studies dipole moments were measured in solutions of too high a concentration, and, consequently, it was not possible to avoid the superposition of the association effect.

The deviation of the experimentally found values of dipole moments from the calculated additive values is explained by the polarization of the imidazole ring in the direction of the C=N bond (V), however, the degree of polarization is too weak to produce an ionic structure.



(IV) (V)

The direction of the moment of the imidazole ring can be determined with the help of the values for the dipole moments of 5-(6)-nitrobenzimidazole (5.95 D), the imidazole ring, and the nitro group (3.95 D). The angle θ between the directions of the moment of the nitro group and the imidazole ring is given by:

$$\theta = \mathrm{Arc\,cos}\,\frac{\mu^2 - \mu^2_{NO_2} - \mu_{HM}}{2\mu_{NO_2}\mu_{HM}} = 9°.$$

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STUDY OF SYNTHETIC PATHWAYS FOR THE PEPTIDE PART OF ERGOT ALKALOIDS*

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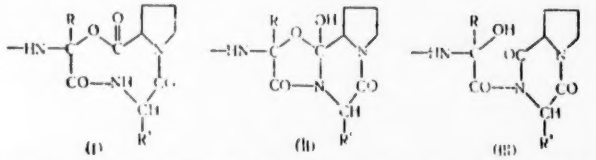
In spite of the large number of studies devoted to the investigation of the chemistry of ergot alkaloids, the structure of the peptide part of these compounds cannot be considered to be proved. It has been established that the peptide part of ergot alkaloids molecules is a tripeptide, the C-terminal amino acid of which is always proline, and the N-terminal amino acid is one of the two α-hydroxy-α-amino acids, viz., α-hydroxyalanine or α-hydroxyvaline. This tripeptide is closed upon itself in a cycle for which two structures have been proposed: the cyclodepsipeptide structure (I) [1], and the cyclol structure (II) [2]. Moreover, we are of the opinion that structure (III) is equally possible, in which diketopiperazine is acylated with the hydroxyamino acid residue. However, one must concede that not a single one of this structures can give a complete explanation of all the reactions occuring with ergot alkaloids molecules under different conditions. It is not excluded, either, that these three forms are capable of interconversition. In particular, the possibility of the transformation of the cyclodepsipeptide form (I) into the cyclol form (II) by means of a transannular reaction of the ester and amide groups has been indicated as early as in 1955 by Cohen and Witkop [3]. At the same time, Grob and Meier [4] were considering the structure (III) as an intermediate formed from the cyclol structure (II) during the thermal dissociation of ergot alkaloids molecules.



(I) (II) (III)

One of the ways of solving the problem of the structure of the peptide part of ergot alkaloids is the synthesis of their peptide residue, as well as the study with model compounds of the possibility of tautomeric or isomeric conversions of the type (I ⇌ II ⇌ III). In connection with this problem, we have synthesized a tripeptide containing the sequence of amino acid residues of ergotamine, viz., N-benzoyl-α-benzyloxyalanylphenylalanylproline, and its analog N-benzoyl-α-benzyloxyglycylphenylalanylproline.

That the synthesis of peptides containing as N-terminal amino acids residues of N-acyl-α-hydroxy-(or α-alkoxy)-α-amino acids is possible, in principle, has been established by us earlier [5], when we made use of the oxazolone method and the method of activated esters for the building up of peptide bonds. Later, we found out that such peptides can also be successfully prepared by the carbodiimide method, the highest yields of peptide esters being obtained when the more stable α-alkoxy-N-acylamino acids were used. The conversion of the mentioned peptide esters to the free acids, in contrast with the peptide esters with a free α-hydroxy group, can be effected by means of alkaline hydrolysis.

These facts induced us to choose N-benzoyl-α-benzyloxyamino acids as starting materials in the present work. This renders possible the transition from peptides containing α-alkoxy-α-amino acids residues to peptides with a free α-hydroxy group by hydrogenolysis. The conditions for the removal of the benzyl group were preliminarily studied on the benzyl esters of N-benzoyl-α-benzyloxyglycine, and N-benzoyl-α-benzyloxyalanine with the result that complete debenzylation was attained at 20-25° and normal pressure in the presence of 10% palladium on charcoal. Under similar conditions, the dipeptide (XA) gave N-benzoyl-α-hydroxyglycyl-L-phenylalanine.

* Preliminary results of these studies were first reported in 1958 at the First Peptide Symposium in Prague and in 1960 at the Third Peptide Symposium in Basel.

Properties and Analytical Data of the Peptides Prepared

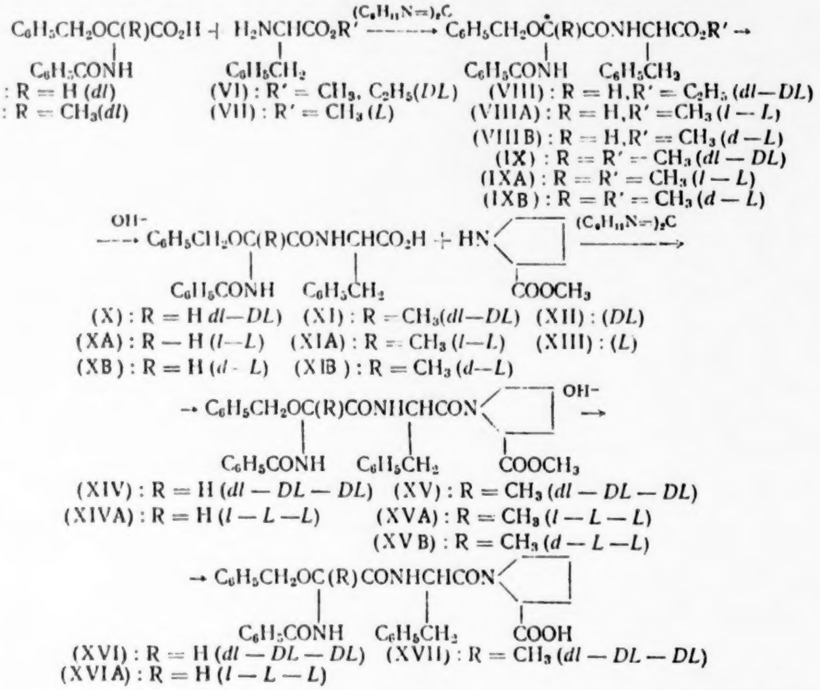
Compound	R	R′	B. p., °C	Crystallization	Yield, %	$[\alpha]_D^{20}$, in EtOH	Calculated, % C	Calculated, % H	Calculated, % N	Found, % C	Found, % H	Found, % N	Mol. wt. (titration) calc.	Mol. wt. (titration) found
bis) Dipeptides of the type $C_6H_5CH_2OC(R)(C_6H_5CONH)CONHCH(CH_2C_6H_5)COOR'$														
VIII	H	C_2H_5	88–91	Needles from EtOH	79				6.08			6.27		
X	H	H	141–144	Needles from AcOEt	84		69.43	5.59	6.47	69.50	5.62	6.42	432	447
IX	CH_3	CH_3	154–156	Needles from EtOH	91		70.42	6.10	6.08	70.23	6.18	6.14		
XI	CH_3	H		Amorphous	76				6.27			6.43	446	435
VIIIA	H	CH_3	143–144	Needles from EtOH	45	−35	69.93	5.87	6.27	70.21	6.07	6.14		
XA	H	H	173–175	Prisms from EtOH	93	−9	69.43	5.59	6.47	69.45	5.71	6.42	432	446
VIIIB	H	CH_3		Amorphous	13	+29	69.93	5.87	6.27	70.15	6.20	6.32		
XB	H	H		Amorphous	80	+36			6.47			6.77	432	437
IXA	CH_3	CH_3	140–141*	Needles from EtOH	46	−6**	70.42	6.10	6.08	70.36	6.18	6.10		
XIA	CH_3	H		Amorphous	95	+5.5	69.93	5.87	6.27	69.66	6.17	6.64	446	450
IXB	CH_3	CH_3	140–141*	Prisms from EtOH	34	+88**	70.42	6.10	6.08	70.76	6.11	5.92		
XIB	CH_3	H	95–97	Prisms from 30% EtOH	80	+147	69.93	5.87	6.27	69.49	5.92	6.22	446	449
Tripeptides of the type $C_6H_5CH_2OC(R)(C_6H_5CONH)CONHCH(CH_2C_6H_5)CON\langle\text{ring}\rangle COOR'$														
XIV	H	CH_3		Oil										
XVI	H	H	176–180	Needles from AcOEt+EtOH	13***		68.03	5.90	7.93	67.94	5.98	7.91	529	532
XV	CH_3	CH_3	157–159	Prisms from EtOH	87		68.92	6.33	7.54	69.16	6.42	7.59		
XVII	CH_3	H		Amorphous	41				7.73			7.92	543	536
XIVA	H	CH_3		Amorphous	90									
XVIA	H	H		Amorphous	49	−58	68.03	5.90	7.93	68.09	6.18	7.75	529	540
XVA	CH_3	CH_3	143–145	Needles from EtOH	51	−36**	68.92	6.33	7.54	69.10	6.35	7.67		
XVB	CH_3	CH_3		Amorphous	85	+26			7.54			7.46		

* The mixed melting point of (IXA) and (IXB) is 121-122°.

** In $CHCl_3$.

*** Yield in two stages, with relation to (X).

The condensation of the racemic N-benzoyl-α-benzyloxy-α-amino acids (IV) and (V) with the esters of DL-phenylalanine (VI) in the presence of dicyclohexylcarbodiimide led to the corresponding racemic dipeptides (VIII) and (IX), which were further hydrolyzed to the acids (X) and (XI). The latter reacted with the ester of DL-proline (XII) to give the esters of the tripeptides (XIV) and (XV), and then the acids (XVI) and (XVII).



The problem of the preparation of peptides containing residues of optically active α-substituted α-amino acids has been successfully solved by condensing the racemic N-acyl-α-benzyloxy-α-amino acids with the ester of the optically active amino acid with a subsequent separation of the diastereoisomers thus formed. Thus, condensation of the racemic N-benzoyl-α-benzyloxyglycine (IV) with the methyl ester of L-phenylalanine (VII) gave a mixture of diastereoisomers, which was fractionated by crystallization from alcohol to the two stereoisomeric esters of the dipeptide (VIIIA) and (VIIIB). Hydrolysis of these two compounds led to the corresponding acids (XA) and (XB). Similarly, compounds (IXA) and (IXB), and, subsequently, (XIA) and (XIB)* were synthesized from racemic N-benzoyl- -benzyloxyalanine (V) and the ester (VII). Condensation of one of the isomeric dipeptides, viz., (XA) with the methyl ester of L-proline (XIII) gave the ester (XIVA), and hydrolysis of the latter gave the corresponding acid (XVIA). In the same manner, the two stereoisomeric dipeptides (XIA) and (XIB) were used to prepare the corresponding tripeptide esters (XVA) and (XVB).

Preparation and Hydrolysis of Peptide Esters

Condensation. A suspension of 0.01 mole of N-benzoyl-α-benzyloxy-α-amino acid, or the dipeptide in CH_2Cl_2 in the case of the preparation of [(VIII), (IX), (XIV), or (XV)], or in tetrahydrofuran [in the case of (VIIIA), (VIIIB), (IXA), (IXB), (XIVA), (XVA), and (XVB)] was treated first with an ethereal solution of the amino acid (VI), (VII), (XII), or (XIII)**(0.01-0.012 mole), and then with dicyclohexylcarbodiimide (0.01 mole) in the same solvent. After 20-25 hr, the reaction mixture was treated with a few drops of glacial acetic acid, and, after standing at 0-5° for

* In so far as a comparison between compounds (VIIIA) and (IXA) on one hand, and (VIIIB) and (IXB) on the other hand shows a positive shift of the optical activity, one can assume that in compounds (VIIIB) and (IXB) the asymmetric carbon atom indicated by an asterisk possesses a (+)-activity, and hence its configuration can be tentatively designated as d. This is why we represent compounds (VIIIB), (IXB), etc., as d-L compounds, and compounds (VIIIA), (IXA), etc., as *l*-L (cf. the scheme and table).

** The methyl esters of DL-proline, L-proline, and L-phenylalanine were obtained in 75-80% yields in the form of their hydrochlorides by the action of $SOCl_2$ on a solution of the appropriate amino acid in methanol (comp. [6]).

1-1.5 hr, was filtered from the precipitated dicyclohexylurea. The solvent was distilled off in vacuum, and the residue dissolved in ethyl acetate or ether. The solution thus obtained was washed, in succession, with 4% $NaHCO_3$, water, 5% HCl, and water, and was then dried with Na_2SO_4. The residue after removal of the solvent by vacuum distillation was either hydrolyzed at once, or crystallized from the convenient solvent (cf. the table). The mixture of diastereoisomeric dipeptides was fractionated by repeated (4-5 times) recrystallization from alcohol. Isomers of the A series were more difficultly soluble in alcohol than those of the B series.

Hydrolysis. A solution or suspension of 0.01 mole of the di- or, tripeptide ester in 25 ml of methanol was treated with 0.015-0.018 mole of 2N NaOH, and the mixture was stirred for 0.5-1 hr at 20-25° in the case of (VIII), (VIIIA), (VIIIB), (XIV), and (XIVA), and at 35-37° in the case of (IX), (IXA), (IXB), and (XV). After addition of 15-20 ml of water, the reaction mixture was filtered, the methanol removed in vacuum, and the unsaponified starting material was extracted from the residue with ether or ethyl acetate. The aqueous solution was then acidified with 10% HCl, and the peptides thus obtained were purified by crystallization (cf. the table), or reprecipitation by addition of hydrochloric acid to their solution in sodium bicarbonate.

Reductive Debenzylation

The substance was hydrogenated in alcoholic solution at 20-25° under normal pressure in the presence of an equal amount (by weight) of 10% Pd/C; the solvent was then removed in vacuum, and the residue titrated with ether and filtered off.

Half a gram of the benzyl ester of N-benzoyl-α-benzyloxyglycine gave 0.22 g (84%) of N-benzoyl-α-hydroxyglycine [7], 0.5 g of the benzyl ester of N-benzoyl-α-benzyloxyalanine gave 0.17 g (71%) of N-benzoyl-α-hydroxyalanine [7], and 0.27 g of N-benzoyl-α-benzyloxyglycyl-L-phenylalanine (XA) gave 0.19 g (90%) of N-benzoyl-α-hydroxyglycyl-L-phenylalanine, m. p. 156-158° (dec.) (from alcohol), mol. wt.: Found (titration), 343; calcd. 342.

Found %: C 63.33; H 5.41. $C_{18}H_{18}O_5N_2$. Calculated %: C 63.12; H 5.29.

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A STUDY OF ISOMERIC OCTALINS

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Octalins have attracted the attention of many investigators. In his well known researches on the stereochemistry of bicyclic compounds, Hückel prepared and studied all the isomeric octalins. Turova-Polyak described the irreversible catalysis of trans-Δ-2,3-octalin on palladized asbestos [1], and Linstead et al., investigated the disproportionation of this hydrocarbon and of Δ-9,10-octalin in the presence of platinum and palladium catalysts [2]. The reaction of octalins with various oxidizing agents has been described several times. Thus, ozonolysis of Δ-9,10-octalin led under certain conditions to cyclodecane-1,6-dione [3-5], which constitutes the starting product for the synthesis of the simplest azulene. Reduction of cyclodecanedione led to cyclodecane-1,6-diol [5]. The same diol has been synthesized from octalin oxide obtained by the oxidation of Δ-9,10-octalin with hydrogen peroxide in formic acid [6]. Octalin oxide has been previously prepared by oxidation of the same hydrocarbon with benzoyl peroxide [3, 7]. Octalins have been used in alkylation [8], acylation [8], hydroformylation [10] and other reactions.

A large space is devoted in researches on octalins to methods of their preparation and identification. In many cases synthesis leads to mixtures of isomers scarcely differing in properties. It is not always possible to surmount the difficulties encountered in the fractionation of such mixtures, and this explains the discrepancies in the descriptions of individual octalins given by different authors. It is too early to speak of any general method for the analysis of octalins. Until recently, the identification of octalins was achieved mostly by the nitrosochlorination and oxidation reactions. The nitrosochloride of Δ-9,10-octalin (9-chloro-10-nitrosodecalin) appears as pale blue crystals melting at 91°; it can be prepared in good yield, and it is easily separated by solution in acetone from the white nitrosochlorides of cis-Δ-2,3- and Δ-1,9-octalins which are formed simultaneously in small amounts. The latter products melt with decomposition, the first at 186°, and the other at about 121-135°, or 142-143°, depending on the rate of heating.

Not unfrequently octalins are identified by their oxidation to the corresponding carboxylic acids, followed by melting point determination. In investigations on the structures of cis-Δ-1,2- and Δ-1,9-octalins, some authors made use of oxidative hydrolysis with osmium tetroxide, leading to the formation of crystalline decalin-diols [11,12]. For the determination of the position of the double bond in Δ-9,10-octalin, this hydrocarbon was oxidized to octalin oxide, and the oxide was then hydrated to the corresponding glycol; the latter was dehydrated to hexalin [7].

Spectral methods were relatively little used in the study of octalins. Infrared spectra of cis- and trans-Δ-1,2-octalins, and Δ-1,9- and Δ-9,10-octalins were recorded by Cope [12]. Spectra of cis-Δ-2,3-octalin in the ultraviolet region were studied by S. Kimura [13], and the Raman spectra of trans-Δ-2,3-octalin by Kohlrausch [14]. Hückel and Fechtig determined Δ-1,9- and Δ-9,10-octalins in mixtures with the help of the ultraviolet spectra of their complexes with iodine [15].

In the present work, we studied the Raman spectra of cis-Δ-2,3-octalin, Δ-9,10-octalin, and a mixture of Δ-1,9- and Δ-9,10-octalins.

EXPERIMENTAL

The starting material for the preparation of octalins was cis-cis-decalin-2-ol, m. p. 103°, which was isolated from a mixture of its isomers by filtration and recrystallization from ligroin. Cis-Δ-2,3-octalin was prepared by the dehydration of this decalol, while Δ-9,10-octalin was obtained as a result of the isomerization occuring during dehydration. The formation of Δ-9,10-octalin during the dehydration of a mixture of decalols in the presence of zinc chloride was demonstrated by Hückel [3]. Linstead obtained this hydrocarbon during the dehydration of trans-decalin-2-ol in the presence of a mixture of orthophosphoric acid and phosphoric anhydride [16]. At the same time, it was shown that trans-Δ-2,3-octalin easily isomerizes with the formation of Δ-9,10-octalin.

We prepared Δ-9,10-octalin by gradually heating to 200°, with mechanical stirring, a mixture of 200g of cis-cis-decalin-2-ol and 70 g of orthophosphoric acid, allowing a continuous distillation of the reaction products. The yield of hydrocarbons was 106 g (61%); these were boiled for 2 hr over metallic sodium in order to remove unreacted decalol. The product thus obtained was distilled over sodium; it had b. p. 188-189° (767 mm), d^{20}_4 0.9076, $n^{20}D$ 1.4940, and mol. wt. 134. By the action of isoamyl nitrate and hydrochloric acid, at −10°, 5.5 ml of this substance gave 2.3 g (31%) of nitrosochlorides. Fractionation of the latter with acetone led to the isolation of 0.1 g of white crystals m. p. 125-127°, and 2 g of pale blue crystals, m. p. 90°. The data obtained show that under the stated experimental conditions the Δ-2,3-octalin produced is partially converted into Δ-9,10- and Δ-1,9-octalins.

Pure Δ-9,10-octalin was isolated from the mixture of octalin isomers through the formation of nitrosochlorides. The pale blue crystals obtained in a series of experiments, and recrystallized from acetone were decomposed by Hückel's method [3] to 18 ml of octalin. The purified product boiled over sodium metal at 193.5-195° (758 mm); it had d^{20}_4 0.9170, $n^{20}D$ 1.4992, and aniline point (1:1) below −30°. Tentative determinations showed that the solubility of the nitrosochlorides in acetone is 1:10 in the case of the blue product, and 1:1000 in the case of the white products. Therefore, the content of related isomers in Δ-9,10-octalin does not exceed 1-2%.

For the preparation of cis-Δ-2,3-octalin we first studied the dehydration of decalol in the presence of the cation-exchange resin KU-2 (hydrogen form). It is known, that in many cases, the reactions of organic substances over KU-2 occur in a selective manner, without the formation of side-products.

Dehydration experiments were carried out by heating decalol with 20-30% of KU-2 at 140-170° for 2-3 hr. The maximum yield of octalin (55% of the theoretical) obtained in these experiments was attained when decalol was heated with 30% of KU-2 at 165-170° for 3 hr. The octalin freed from decalol boiled over metallic sodium at 191.5-194° (766 mm), and had $n^{20.5}D$ 1.4975. Five and a half grams of octalin gave 1 g (14%) of nitrosochlorides, from which 0.8 g of pale blue crystals melting at 91°, and 0.2 g of white crystals melting at 124-125° were isolated with the help of acetone. It follows that during the dehydration of cis-cis-decalin-2-ol in the presence of KU-2 there occurs a partial isomerization of cis-Δ-2,3-octalin to Δ-1,9- and Δ-2,3-octalins; therefore, this method is unsuitable for the preparation of pure Δ-2,3-octalin for spectroscopic work. Later, we made use of the well known dehydration of decalol in the presence of 200% of freshly fused potassium bisulfate. The mixture was rapidly heated to 190-195° with mechanical stirring and continuous distillation of the reaction products. After drying and removal of decalol, octalin (77.5% of the theoretical) was obtained, boiling at 190-192° (770 mm), and having d^{20}_4 0.9152, $n^{20}D$ 1.4967, and aniline point (1:1) at −3°. From 5.5 ml of this product, 0.4 g of a very pale blue mixture of nitrosochlorides was obtained. After washing with acetone, this mixture gave white crystals melting at 176°. It was not possible to isolate the blue nitrosochlorides from the acetone washings, as they were present in negligible amount. Oxidation of octalin with an alkaline solution of potassium permanganate gave a crystalline product melting at 159°, a temperature which corresponds to the m. p. of cis-cyclohexanediacetic acid-1,2. One may consider that the cis-Δ-2,3-octalin thus prepared contains only traces of Δ-9,10-octalin.

We recorded the Raman spectra of Δ-9,10-octalin and cis-Δ-2,3-octalin prepared as described above, as well as the spectrum of a mixture of Δ-1,9- and Δ-9,10-octalins, obtained by the dehydration of cis-cis-decalin-2-ol in the presence of orthophosphoric acid.

The spectra were recorded and studied by the standard methods and apparatus, viz., a ISP-51 spectrograph with a 270 mm chamber, a 8 ml cell for taking spectra, and a IZA-2 comparator. All the spectra were taken with strictly the same exposure time, and with the same working conditions of the bulb.

The table gives the frequencies of the Raman lines, and (between brackets) the visually estimated intensities on a 10 point scale. The estimation of the intensity of the lines in the spectrum of each compound was carried out in comparison with the 1684 cm^{-1} line in the spectrum of Δ-9,10-octalin, the intensity of this line being taken as 10 units. The intensity of the lines in the region of the valency vibrations of the C−H bond was not estimated.

It appears from the table that in the spectrum of Δ-9,10-octalin there is only one intense line at about 1684 cm^{-1} in the region of the valency vibrations of the C=C bond; in the spectrum of cis-Δ-2,3-octalin there is one intense line with a frequency of 1652 (8) cm^{-1}, and another less intense line with a frequency of 1685 (2) cm^{-1}. In the mixture of Δ-9,10-octalin and Δ-1,9-octalin, three lines with the frequencies of 1656 (1), 1672 (2), and 1686 (7) cm^{-1} are observed.

By taking into account the sensitivity of the method of Raman spectra, and also the fact that the Δ-9,10-octalin we have prepared could not contain more than 1-2% of other isomers, it may be safely said that the spectrum of

Δ-9,10 is free of lines due to impurities. This is also confirmed by the relatively small number of lines in the spectrum of this compound.

Frequency of the Raman Lines of Octalins (in cm^{-1})

Δ-9,10-octalin	Cis-Δ-2,3-octalin	Δ-1,9- and Δ-9,10 octalins	Δ-9,10-octalin	Cis-Δ-2,3-octalin	Δ-1,9- and Δ-9,10-octalins
316 (1) s*	316 (1) s	318 (1) s	1043 (1)	1046 (5)	1045 (3)
360 (0)	355 (0)	357 (0)	1078 (7)	1072 (6) bkg	1079 (4) bkg
	376 (6)	375 (1)	1098 (4)	1109 (3) bkg	1107 (3) bkg
	382 (6)	385 (1)	1132 (3) bkg*	1130 (3) bkg	1128 (1) bkg
418 (8)	420 (2) dif*	418 (6)		1158 (3) bkg	
456 (1)			1182 (8)	1177 (4) bkg	1180 (5) bkg
	475 (2)	473 (1)		1200 (0)	
	497 (2)	498 (1)		1221 (3)	1220 (2
509 (2)		511 (1)		1240 (5) bkg	1243 (3) bkg
542 (2)	538 (0)	540 (1)		1254 (5) bkg	
	573 (3)	579 (1)	1261 (1)	1266 (5) bkg	1266 (5 bkg
		599 (2)	1270 (7)		
620 (0)	318 (1)			1288 (2)	
	664 (4)			1332 (4 bkg	1332 (2) bkg
675 (8)		676 (5)	1356 (2)		1345 (3 bkg
	694 (3)				1357 (2,
	728 (6)	728 (3)	1375 (3)	1376 (1 bkg	1378 (1)
		748 (4)	1434 (10)	1442 (10) s	1438 (10)
	774 (5)	772 (1)	1449 (6)		1451 (8)
808 (3)		809 (0)	1464 (6)		
830 (4)	834 (0)	833 (0)		1652 (8)	1656 (1)
	846 (3)				1672 (2)
		859 (3)	1684 (10)	1686 (2)	1686 (7)
	872 (2)		2838	2838	2835
884 (7)	881 (2)	886 (4)	2860	bkg	2858
895 (4)	896 (3)	896 (2)	2902	bkg	2898
	935 (0)	933 (0)	2941	2938	2938
	966 (4)	965 (0)		3020	3022
988 (6)	986 (3)	988 (3)			
		1014 (1)			

* S – sharp; dif – diffuse; bkg – background.

The spectrum of cis-Δ-2,3-octalin may contain the frequencies of Δ-9,10-octalin, as the preparation of the nitrosochlorides of cis-Δ-2,3-octalin yielded traces of the nitrosochlorides of Δ-9,10-octalin. The spectrum of the mixture displays the lines due to all the three isomers.

By taking all these considerations into account, one can attribute the observed frequencies of the valency vibrations of the C=C bond to the different compounds in the following manner:

The frequency of the valency vibration of the C=C bond equal to 1684 cm^{-1} belongs to Δ-9,10-octalin. the frequency equal to 1672 cm^{-1} belongs to Δ-1,9-octalin, and the one of 1652 cm^{-1} belongs to cis-Δ-2,3-octalin.

On the basis of the observed vibration frequencies of the C=C bond in the octalins investigated, one can consider that the 9,10 bond is stronger than the 1,9 bond, which is in turn stronger than the 2,3 bond.

This conclusion is in agreement with the observed phenomenon of isomerization of cis-Δ-2,3-octalin to Δ-1,9- and Δ-9,10-octalins. Cases of reversible isomerization are unknown.

The spectrum of Δ-9,10-octalin contains an intense line at about 675 cm^{-1} which is missing in the spectrum of cis-Δ-2,3-octalin. The intensity of this line is considerably lowered in the mixture. Apparently this line is characteristic for Δ-9,10-octalin. Lines at 418 and 830 cm^{-1} also stand out by their intensity in the spectrum of Δ-9,10-octalin.

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HOMOLYTIC ISOMERIZATION OF 1-FLUORO-1,1-DICHLORO-2-BROMOPROPENE

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As shown earlier [1], 1,1,1-trichloro-2-bromopropene easily isomerizes by a chain radical mechanism to 1,1,2-trichloro-3-bromo-1-propene. The following scheme is proposed for this isomerization:

$$\begin{array}{l} \dot{Br} + CH_2 = CBrCCl_3 \rightarrow \underset{A}{BrCH_2\dot{C}BrCCl_3} \\ A \xrightarrow{\text{rearr.}} \underset{A'}{BrCH_2CBrCl\dot{C}Cl_2} \\ A' \longrightarrow BrCH_2CCl = CCl_2 + \dot{Br} \end{array} \qquad (I)$$

Upon irradiation of the substance with ultraviolet light, this isomerization proceeds so rapidly that one does not succeed in capturing the intermediate radicals A and A' even with such an effective chain reaction carrier as hydrogen bromide (i.e., the reactions A + HBr $\rightarrow CH_2BrCHBrCCl_3$ + Br and A' + HBr $\rightarrow CH_2BrCClBrCCl_2H$ + Br do not take place).

The introduction of fluorine in the trichloromethyl group, as shown in the preceding publication [2] considerably retards the rearrangement of the radical $CCl_2F\dot{C}HCH_2Br \rightarrow \dot{C}ClFCHClCH_2Br$ with the result that during the ultraviolet light catalyzed addition of hydrogen bromide to $CCl_2FCH = CH_2$ two reaction products are formed: $CH_2BrCH_2CCl_2F$ and $CH_2BrCHClCHFCl$ (in this reaction 1,1,1-trichloropropene gives only the rearranged $CHCl_2CClHCH_2Br$).

In the present work we studied some reactions of 1-fluoro-1,1-dichloro-2-bromopropene which is an analog of 1,1,1-trichloro-2-bromopropene. Upon standing, 1-fluoro-1,1-dichloro-2-bromopropene undergoes dimerization (the table, expt. 5). As shown below, the dimer consists basically of $BrCH_2CBr(CCl_2F)CH_2CCl = CClF$, the formation of can be explained with the help of the following reactions:

$$\begin{array}{l} Br + CH_2 = CBrCCl_2F \rightarrow \underset{Б}{CH_2Br\dot{C}BrCCl_2F} \\ Б + CH_2 = CBrCCl_2F \rightarrow \underset{В}{BrCH_2CBr(CCl_2F)CH_2\dot{C}BrCCl_2F} \\ В \xrightarrow{\text{rearr.}} \underset{В'}{BrCH_2CBr(CCl_2F)CH_2CBrCl\dot{C}ClF} \\ В' \rightarrow BrCH_2CBr(CCl_2F)CH_2CCl = CClF + Br \end{array} \qquad (II)$$

Heating of the starting fluorodichlorobromopropene (table, expts. 1 and 2) leads to the synthesis of the dimer, as well as to isomerization with the formation of 1-fluoro-1,2-dichloro-3-bromo-1-propene according to a scheme analogous to scheme (I). These reactions are speeded up by the addition of small amounts of benzoyl chloride, and are retarded by the addition of hydroquinone (table, expts. 3 and 6).

Carrying this reaction out under ultraviolet light in the presence of an excess of hydrogen bromide led to the formation of only small quantities of the dimer; moreover, 1-fluoro-1,1-dichloro-2,3-dibromopropane (main reaction

product), and 1-fluoro-1,2-dichloro-3-bromo-1-propene were produced (table, expt. 7). Thus, radical B formed in the course of the reaction was prevented from reacting further by giving a reaction product with hydrogen bromide, a bromine atom being regenerated:

$$B \xrightarrow{HBr} CH_2BrCHBrCCl_2F + Br.$$

No.	Condition of the reaction	time in hr	$n^{20}D$ of the final mixture	Yield of the products: $CFCl_2-CBr=CH_2$, in g	$CFCl=CClCH_2Br$**, in g	$CFCl=CClCH_2Br$**, in the % of theoretical w.r. to the product which had reacted	Dimer***, in g
1	90°	6	1.4860	11.2	3.7	42	4.2
2	140°	6	1.5040	5	6.4	42	7.5
3	90° + Bz_2O_2	6	1.5000	6.9	6	46	6.4
4	Irradiation with ultraviolet light	6	1.4870	13.2	2.4	34	4
5	Room temperature	5 days	1.5010	9			9.1
6	90° + hydroquinone	6	1.4740	19.1	–	–	–
7	Addition of HBr and irradiation with ultraviolet light (40-50°)****	7	–	10	0.9	3	2.7

* Experiments were carried out with 20 g of fluorodichlorobromopropene; Expt. 7, with 40 g of this substance.

** 1-Fluoro-1,2-dichloro-3-bromopropene obtained in all these experiments gave the same values, viz.: 58° for 35 mm, $n^{20}D$ 1.5000, d^{20}_4 1.8461; MR 33.15, calculated MR 32.98.

Found %: C 17.23, 17.14; H 0.96, 0.98; F 9.17, 9.26. Calculated %: C 17.33; H 0.97; F 9.14.

The picrates of the diethylamine derivatives of these fluorodichlorobromopropenes had m. p. 101-102°, and did not give a m. p. depression with the picrate obtained by an independent method (cf. following experiments).

*** The dimer, as isolated in all these experiments has the same characteristic values, viz.: b. p. 110°, for 3 mm, $n^{20}D$ 1.5410, d^{20}_4 2.0605; MR 63.80, calculated MR 64.23. Found mol. wt. 409.5; calculated 415.7 (cryoscopically in benzene).

Found %: C 17.30, 17.39; H 1.03, 0.99; F 9.12, 9.24. Calculated %: C 17.33; H 0.97; F 9.14.

The infrared spectrum of the dimer (taken in the optical laboratory of the Institute of Heteroorganic Compounds, Academy of Sciences, USSR by N. V. Chumaevskii) contains an intense absorption band at 1670 ± 5 cm^{-1}, characteristic for compounds containing the CFCl = CCl group [4].

**** The main reaction product (32 g) is 1-fluoro-1,1-dichloro-2,3-dibromopropane, b. p. 80-81° for 17 mm, $n^{20}D$ 1.5175, d^{20}_4 2.1536. Its dehydrobromination led to the starting 1-fluoro-1,1-dichloro-2-bromopropene.

The absence of $CH_2BrCClBrCClFH$ – the reaction product of the rearranged radical B' with HBr according to scheme (III) – in the reaction mixture, and the presence of $CH_2BrCCl = CClF$ produced according to scheme (IV):

$$B \xrightarrow{rearr.} \underset{Б'}{CH_2BrCClBr\dot{C}ClF} - \begin{cases} \xrightarrow{HBr} CH_2BrCClBrCClFH + Br & \text{(III)} \\ \longrightarrow CH_2BrCCl = CClF + Br & \text{(IV)} \end{cases}$$

indicate the considerably higher rate of the elimination reaction in the case of this radical [scheme (IV)], as compared with the substitution reaction with hydrogen bromide. This result allows to assume that another possible pathway for dimer formation, namely, via radical B' according to scheme (V):

$$BrCH_2CClBr\dot{C}ClF \xrightarrow{+CH_2=CBrCCl_2F} BrCH_2CBrClCClFCH_2\dot{C}BrCCl_2F \quad (V)$$

and then as in scheme (II) with the formation of the dimer of normal structure $BrCH_2CBr \cdot ClCClFCH_2CCl = CClF$, is scarcely probable, as the rate of this reaction under the given conditions must be apparently lower than the reaction rate of B' with hydrogen bromide,* and therefore, lower than the elimination reaction rate. Thus, radical B' can give under the studied conditions only 1-fluoro-1,2-dichloro-3-bromo-1-propene.

The structure of the starting 1-fluoro-1,1-dichloro-2-bromopropene prepared according to the scheme:

$$CCl_2FCH = CH_2 + Br_2 \rightarrow CCl_2FCHBrCH_2Br \xrightarrow{KOH} CCl_2FCBr = CH_2 \quad (VI)$$

was proved by ozonolysis, which gave formaldehyde and fluorodichloroacetic acid.

The structure of 1-fluoro-1,2-dichloro-3-bromo-1-propene was established by the following reactions:

$$CClF = CCl - CH_2Br \xrightarrow{NH(C_2H_5)_2} CClF = CCl - CH_2N(C_2H_5)_2 \xleftarrow{KOH}$$

$$CClF = CHCH_2Cl \rightarrow CClF = CHCH_2N(C_2H_5)_2 \xrightarrow{Cl_2} CCl_2FCHClCH_2N(C_2H_5)_2$$

The amines obtained in both ways were identified by their picrates.

1-Fluoro-1,1-dichloro-2,3-dibromopropane obtained by the addition of HBr to 1-fluoro-1,1-dichloro-2-bromopropene is identical in all its properties with the dibromide obtained in reaction (VI). Moreover, its dehydrobromination with alcoholic alkali gave the starting fluorodichlorobromopropene:

$$CCl_2FCHBrCH_2Br \rightarrow CCl_2FCBr = CH_2.$$

The structure of the dimer $BrCH_2CBr(CCl_2F)CH_2CCl = CClF$ has been confirmed by several experimental data. Thus, its infrared spectrum shows the presence of a $FCCl = CCl$ group; furthermore, it reacted with Zn in alcohol to give a diene $C_6H_4Cl_4F_2$, which led to formaldehyde and a carbonyl derivative (not isolated in the pure state) upon mild ozonolysis. Under more drastic conditions (heating with a large excess of zinc for 8 hr on a boiling water-bath), elimination of two bromide atoms is accompanied by reduction at the expense of one or two chlorine atoms with the formation of dienes of the composition $C_6H_5Cl_3F_2$, and $C_6H_5Cl_2F_2$. Ozonolysis of these dienes leads also to formaldehyde.

EXPERIMENTAL

1-Fluoro-1,1-dichloro-2,3-dibromopropane was obtained with an 80% yield by the bromination of 1-fluoro-1,1-dichloropropene in glacial acetic acid; b. p. 80° for 17 mm, $n^{20}D$ 1.5175, d^{20}_4 2.1540; MR 40.60, calculated MR 41.21.

Found %: C 12.48, 12.54; H 1.17, 1.08. Calculated %: C 12.47; H 1.05.

By reacting with diethylamine, it gave, with a 73% yield, 1-fluoro-1-chloro-2-bromo-3-diethylamino-2-propene; b. p. 85-86° for 20 mm, n^{20}_4 1.4710, d^{20}_4 1.3591; MR 50.30, calculated MR 50.53.

Found %: C 34.42, 34.48; H 4.81, 5.06. Calculated %: C 34.37; H 4.94.

The picrate of the diethylamine derivative had m. p. 121-122° (from alcohol).

1-Fluoro-1,1-dichloro-2-bromopropene was prepared with a 65% yield by the dehydrobromination of 1-fluoro-1,1-dichloro-2,3-dibromopropane with potassium hydroxide in ethyl cellosolve. After a double distillation, it had b. p. 53° for 70 mm, $n^{20}D$ 1.4740, d^{20}_4 1.7905; MR 32.70, calculated MR 32.98.

Found %: C 17.23, 17.18; H 1.02, 1.08. Calculated %: C 17.33; H 0.97.

* In [2] we have shown that the radical $BrCH_2CHClCClF$ having a related structure reacts under similar conditions almost exclusively with the removal of H from HBr, but not by addition to the olefin ($CH_2 = CHCCl_2F$).

Ozonolysis of this fluorodichlorobromopropene, followed by decomposition of the ozonide with water led to formaldehyde (isolated as a dimedon derivative, m. p. 189°, mixed m. p. with an authentic sample, 189°), and fluorodichloroacetic acid, b. p. 162°, reported m. p. [3], 162.5°; its anilide melted at 75° (from heptane).

Found %: C 42.96, 43.00; H 2.78, 2.83; F 8.12, 8.56. Calculated %: C 43.27; H 2.72; F 8.56.

Reactions of 1-fluoro-1,1-dichloro-2-bromopropene. Data concerning reactions of fluorodichlorobromopropene are included in the table.

Preparation of the picrate of 1-fluoro-1,2-dichloro-3-diethylamino-1-propene. a) 1-Fluoro-1-chloro-3-diethylamino-1-propene was obtained from 1-fluoro-1,3-dichloro-1-propene by the method described in [1]; yield, 73%, b. p. 87° for 100 mm, $n^{20}D$ 1.4320, d^{20}_4 1.0119; MR 42.46, calculated MR 42.76.

Found %: C 50.65, 50.70; H 8.05, 7.90; F 11.52, 10.83. Calculated %: C 50.75; H 7.91; F 11.47.

Picrate m. p. 85-86° (from alcohol).

b) 1-Fluoro-1,1,2-trichloro-3-diethylaminopropane was obtained by the chlorination of 1-fluoro-1-chloro-3-dimethylamino-1-propene; yield 74%, b. p. 64-65° for 2 mm, $n^{20}D$ 1.4540, d^{20}_4 1.2200; MR 52.40, calculated MR 52.96.

Found %: C 35.65, 35.69; H 5.67, 5.66; F 8.23, 8.13. Calculated %: C 35.54; H 5.54; F 8.05.

Picrate m. p. 152-153° (from alcohol).

c) 1-Fluoro-1,2-dichloro-3-diethylamino-1-propene was obtained by dehydrochlorination of 1-fluoro-1,1,2-trichloro-3-diethylaminopropane with alcoholic potassium hydroxide; yield 91%, b. p. 66-67° for 15 mm, $n^{20}D$ 1.4520, d^{20}_4 1.1400; MR 47.22, calculated MR 47.66.

Found C: 41.83, 41.73; H 6.19, 6.20; F 8.97, 9.05. Calculated %: C 42.04; H 6.05; F 9.50.

Picrate m. p. 101-102° (from alcohol).

Debromination of the Dimer

To 4 g of zinc dust in 10 ml of absolute ethanol (activated by heating with 0.1 ml of hydrobromic acid and 0.1 ml of acetic acid) was added, dropwise, 22 g of the dimer in 40 ml of absolute ethanol; the mixture was then heated at 50° for 6 hr. The precipitate formed was filtered off and washed with chloroform. The filtrate was acidified with hydrochloric acid, and extracted with chloroform. The chloroform extract was dried over $CaCl_2$, and the residue left after removal of the solvent by distillation, was distilled in vacuum giving 4.2 g of bromine-free diene (31%), b. p. 95° for 35 mm, $n^{20}D$ 1.4710, d^{20}_4 1.4844; MR 48.19, calculated MR 48.23.

Found %: C 28.42, 28.36; H 1.79, 1.80. Calculated %: C 28.16; H 1.86.

Recovered diene: 11.5 g, b. p. 110° (3 mm), $n^{20}D$ 1.5410.

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THE SECONDARY AROMATIC POLYCYCLIC STRUCTURE OF LIGNIN

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(Presented by Academician A. A. Balandin, December 7, 1960)
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The structure of the diverse condensation products of phenylpropane monomers formed during lignin biosynthesis has not yet been completely elucidated. However, one may take it to be a proven fact that the polycyclic aromatic structure exists although to a very small degree, in natural lignin from plate tissue [1, 2]. Oxidation of wood meal with alkaline permanganate [3] leads to the formation of benzene polycarboxylic acids with a 0.14% yield with relation to lignin. Although the yield of these acids is small, the very possibility of their production (mainly of benzene pentacarboxylic acid) proves that natural lignin contains a small amount of condensed rings. Lignin prepared by the acid or the alkaline method, which has been thus submitted to influences favoring condensation gives a higher yield of benzene polycarboxylic acids upon oxidation with alkaline permanganate. Thus, periodate lignin, heated to 160° at pH 2.2, gave, upon oxidation, 5.15% of benzene pentacarboxylic and 0.57% of benzene tetracarboxylic acids [3]. Hydrolytic lignin treated with alkali at 270° for 1.5 hr gave upon oxidation with alkaline permanganate a still higher yield of benzene polycarboxylic acids isolated as barium salts [4].

Mellitic acid has not been isolated from the oxidation products of natural lignin. The possibility of its preparation [3, 5-7] from technical lignins in small yield (0.2-0.4%), though it cannot constitute a rigid proof for the presence of carbon hexagonal lattices in the structure of these products [8], proves nevertheless without doubt the existence of a starting material for the hexasubstituted benzene in the macromolecule.

The isolation of benzene polycarboyxlic acids from technical lignins, as well as the elucidation of the relation between the formation of these products and the conditions of hydrolysis are necessary for understanding and evaluating the structural changes which occur during the technochemical treatment of wood. This is also important for the investigation of new ways for the chemical utilization of lignin, as benzene polycarboxylic acids constitute a starting material for the synthesis of valuable polyesters, glues, and plastics.

Spruce saw-dust extracted with acetone and passed through a No. 3 sieve was used in the experiments. Acetone was removed by prolonged boiling with water. Samples of wood pulp containing 30.5% of lignin were treated for 6 hr with sulfuric acid (0.5 and 1%) in an autoclave at 160, 180 and 200°. The liquid-solid ratio was 15:1. The samples of lignin obtained under different conditions of hydrolysis were washed to remove the acid, sugars, and humic products, dried, analyzed, and oxidized with alkaline permanganate at 80° for 22 hr [4]. The acids formed were separated as barium salts. To get rid of oxalic acid, the salts were boiled for 12 hr with concentrated nitric acid (sp. gr. 1.52). The latter was removed in vacuum, and the residue thus obtained was extracted first with chloroform to remove the nitrophenols, and then with ether. The ethereal extract yielded a white, solid, partly crystalline mass of a mixture of benzene polycarboxylic acids. These acids were easily soluble in water, alcohol, ether and acetone, and insoluble in benzene and chloroform. Acid equivalent of the acids: 60.2. Fractional crystallization, first from a nitric acid solution, and then from a hydrochloric acid solution allowed to isolate mellitic and benzene pentacarboxylic acid. The former was isolated as ammonium mellitate, and was purified through its copper salt [13]. Treatment with hydrogen sulfide regenerated the free acid which was recrystallized from water. However, in spite of the fact that the acid was repeatedly recrystallized, it was not possible to obtain a completely pure sample by this method. The analytical values for mellitic acid were:

Found %: C 42.3; H 2.40. Calculated %: C 42.1; H 1.75.

Those of benzene pentacarboxylic acid were:

Found %: C 44.24; H 2.13. Calculated %: C 44.29; H 2.01.

Benzene pentacarboxylic acid melts in a sealed capillary tube at 241-242° (dec.); reported m. p. [2]: 239-244°.

TABLE 1. Characteristics of Lignin and Yield of Benzene Polycarboxylic Acids Produced During Oxidation with Alkaline Permanate

No.	Conditions of hydrolysis		Characteristics of lignin		Yield of benzene polycarboxylic acids with relation to lignin, %
	H_2SO_4, %	temp., °C	OCH_3, %	OCH_3, %	
1	0,5	160	7,05	50,98	1,41
2	0,5	180	9,72	85,13	3,20
3	0,5	200	10,02	96,05	10,20
4	1,0	160	8,69	60,18	4,60
5	1,0	180	10,26	92,50	7,90
6	1,0	200	10,08	94,35	12,20

Data pertaining to the oxidation of lignin are given in Table 1.

The actual yield of acids is considerably higher, as great losses occur during the precipitation and washing of barium salts; moreover, ether does not extract benzene polycarboxylic acids completely.

It was interesting to check to what extent a manufactured hydrolytic lignin was capable of undergoing further condensations. Lignin from pine wood meal produced by the glucose section of the Kan hydrolytic factory had been used for this purpose. This product was washed to remove acids, and freed from resins by a prolonged extraction with acetone, following by boiling with water to remove the organic solvent. Then, lignin was submitted to a further condensation treatment in an autoclave with 5% sulfuric acid at 195-198° for 6 hr. The starting product contained 92.53% of lignin, 9.68% of OCH_3, and 0.84% of ash. The final product gave 98.40%, 11.78%, and 0.52%, respectively. Lignin samples were milled for 15 min in a M-10 vibration mill.

One hundred grams of lignin was covered with a tenfold amount of nitric acid (sp. gr. 1.35) and the mixture was kept at 20° for 4 days. Then, the whole product was refluxed on a water-bath for 2.5 hr. The mixture was filtered and the solution thus obtained was left to stand at 0° to allow fractional crystallization to take place and to remove oxalic acid, which separated out. The latter melted after purification at 189°. The filtrate was freed from nitric acid in vacuum, and the residue was extracted for 4 hr with chloroform, which dissolved nitrophenols. Finally, the product was boiled for 12 hr with a tenfold amount of concentrated nitric acid (sp. gr. 1.52) in order to decompose the remaining oxalic acid, and to liberate the benzene polycarboxylic acids. At this stage, samples of condensed lignin give a rapidly precipitating insoluble cream-colored deposit (yield up to 2.3% wt. rel. to lignin). This product was dissolved in a small volume of hot water, and the solution was poured into a concentrated aqueous solution of ammonium hydroxide (sp. gr. 0.89) at 0°; thereby well formed white crystals of ammonium mellitate separated out. This was converted into the silver salt which was used to prepare, by its reaction with methyl iodide, the hexamethyl ester of mellitic acid. After recrystallization from benzene, this ester melted at 182.5°; reported m. p. 183° [7] and 187° [2]. Analytical values for mellitic acid hexamethyl ester:

Found %: C 52.2; H 4.52. Calculated %: C 50.7; H 4.22.

We assume that the ammonium salt of benzene pentacarboxylic acid is partly precipitated together with ammonium mellitate, as such a case has already been described [14].

After the precipitate of mellitic acid was separated out, the nitric acid was removed in vacuum, and the residue was treated with a few ml of formic acid to remove all traces of nitric acid. The sticky thick orange-red mass thus obtained was submitted to prolonged drying in a vacuum dessicator at 50°. The resulting product appeared as a reddish-yellow highly hygroscopic powder, soluble in water, ether, alcohol, acetone, and methyl ethyl ketone, and insoluble in benzene and chloroform. The mean equivalent of the acids obtained was 84. Conductometric titration curves showed the presence of 3-4 acids with different strengths. Apparently, the product was a mixture of monocyclic benzene polycarboxylic acids, and acids with high molecular weights having a more complicated polycyclic structure. Moreover, the product possibly contained nitrogenous substances and tarry admixtures which gave the product its dark color [9]. This complicated mixture was submitted to further oxidation with alkaline permanganate, followed by treatment with nitric acid (sp. gr. 1.52). In this way, almost white readily crystallizable acids were

obtained from the reddish-brown powder. By chromatography, it was shown that these acids consist mainly of hexa-, penta-, and tetracarboxylic acids [10]. One may assume that oxidation of condensed lignin with nitric acid leads to the formation of benzene polycarboxylic acids. From the nitrophenol fraction, obtained with a 3.9% yield, picric acid melting at 121.5° was isolated:

Found %: C 31.97; H 1.44; N 18.45. Calculated %: C 31.44; H 1.31; N 18.34.

The yield of picric acid from condensed lignin (1.8%) was determined by the method of selective precipitation of nitron picrate from acid aqueous media [15]. Table 2 gives the results of a few parallel experiments on the oxidation of lignin with nitric acid.

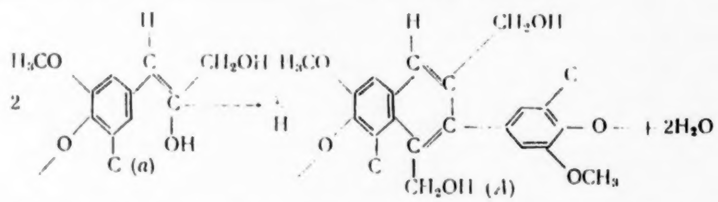
TABLE 2

Substance	Yield with relation to lignin, %			
	oxalic acid	mellitic acid	mixture of benzene polycarboxylic acids	nitrophenols
Starting pine wood lignin supplied by the factory	16-18	not detected	15-17	not determined
Condensed lignin	24-25	2.0-2.3	30-32	3.92

Data on the oxidation of lignin preparations with alkaline permanganate and nitric acid show that condensing agents provoke in this product the formation of a secondary polycyclic aromatic structure, the presence of which may explain the formation of significant amounts of benzene polycarboxylic acids. As a result of condensation, as it appears from the analysis of the starting materials, lignin does not lose its basic methoxylated aromatic ring, but acquires secondary aromatic structures, apparently at the expense of propane side-chains.

Kratzl [1] has shown that the various lignin preparations isolated with the help of acids (e.g., Willstätter's or Schöller's lignins) give Gibbert's ketones upon ethanolysis (it is true, with a considerably smaller yield than natural lignin). This author has confirmed experimentally the relative stability of the side chain of lignin.

It is known that the guaiacylglycerol-β-arylether structure [11] most frequently met with in natural lignin forms, by oxidative hydrolysis, a derivative of hydroxyconiferyl alcohol (a). It is possible to propose as a working hypothesis the following scheme for the condensation of this reactive product:



A similar or analogous type of condensation, probably starts (during the isolation of lignin from plant tissue by treatment with acids) with the formation of α-β- or α-$α_1$-carbon bonds between the propane side-chains [12] and leads to the formation of products of the phenylnaphthalene type (A). By condensation of such a type, an aromatic polycyclic structure may become accumulated to a smaller or greater degree in lignin. The relative content of this structure in the macromolecule depends, as shown, on the conditions of lignin condensation.

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6-AZACYTIDINE AND ITS DERIVATIVES

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Synthetic nucleotides containing anomalous bases related to the purine and pyrimidine constituents of nucleic acids (6-azauracil, mercaptopurine, etc.) are of considerable interest for the study of the biosynthesis of nucleic acids, as well as in their constituting potential cancerostatic and virusostatic preparations. Such compounds are subjected to intensive study in the Institute of Organic Chemistry and Biochemistry of the Czechoslovak Academy of Sciences [1]. In 1957 was achieved the biosynthesis of 6-azauridine (I) [2] having a high anti-tumor activity. It was of interest to synthesize 6-azacytidine (II), as it is known that cytidine is included in nucleic acids considerably easier than uridine [3]. Therefore, one could expect that 6-azacytidine would be a more potent antimetabolite, that is to say, a more powerful inhibitor of the synthesis of nucleic acids.

For the synthesis of 6-azacytidine, we took advantage of the high mobility of the sulfur atom in 4-thio derivatives of pyrimidine nucleosides [4]. The starting material was 6-azauridine, which is now prepared in the Czechoslovak SSR on an industrial scale. By acetylation, 6-azauridine was converted into its peracyl derivatives (tribenzoyl-(III), and triacetyl-(IV) 6-azauridines). Treatment of (I) with a large excess of acetic anhydride led to the formation of tetraacetyl-6-azauridine (V). By the action of phosphorus pentasulfide, the peracyl-6-azauridines were converted into the corresponding peracyl-4-thio-6-azauridines (VI, and VII). Ammonolysis of the substituted 4-thio-6-azauridines led to 6-azacytidine (II) and its derivatives (IX, X, XII).

Heating tribenzoyl-(VI) and tetraacetyl-(VII)-4-thio-6-azauridine with ammonia gave 6-azacytidine (II), m. p. 217-219° (dec.), R_f in system A (n-butanol saturated with water), 0.1 and in system B (isopropanol – ammonia – water, 7:1:2), 0.5.

Found %: C 39.68; H 4.95; N 22.88. $C_8H_{12}O_5N_4$. Calculated %: C 39.33; H 4.92; N 22.93.

6-Azacytidine had been also obtained by the ammonolysis of 4-thio-6-azauridine (VIII), prepared by the debenzoylation of tribenzoyl-4-thio-6-azauridine (VI).

According to literature data, only one hydroxyl group, the one in position 4, is replaced by a sulfur atom [4] when uridine is treated with phosphorus pentasulfide. We obtained spectroscopic confirmation of this fact also in the case of 6-azauridine derivatives. The spectrum of thioazauridine (VIII) obtained by the debenzoylation of tribenzoyl-4-thio-6-azauridine (VI) has λ_{max} at 244 and 332 mμ. On the basis of I. Ionash's data, this corresponds exactly to the spectrum of 4-thio-6-azauracil, whereas 2-thio-6-azauracil displays a λ_{max} at 266 mμ.

By heating tribenzoyl-4-thio-6-azauridine (VI) with n-butylamine, n'-butyl-6-azacytidine (IX) was synthesized [white uncrystallizable form-like material, with R_f values 0.70 (in system A), and 0.78 (in system B)].

Found %: C 47.42; H 7.01; N 18.77. $C_{12}H_{20}O_5N_4$. Calculated %: C 48.00; H 6.71; N 18.66.

The reaction of tribenzoyl-4-thio-6-azauridine (VI) with hydrazine gave different products depending upon the conditions. Were obtained: 1) N'-amino-6-azacytidine (X), as a yellow uncrystallizable foam, with R_f values 0.34 (in system B), 0.39 (in system C, viz., n-butanol – water – acetic acid, 5:3:2), and 0.78 (in system D, viz., methyl cellosolve – water, 8:2).

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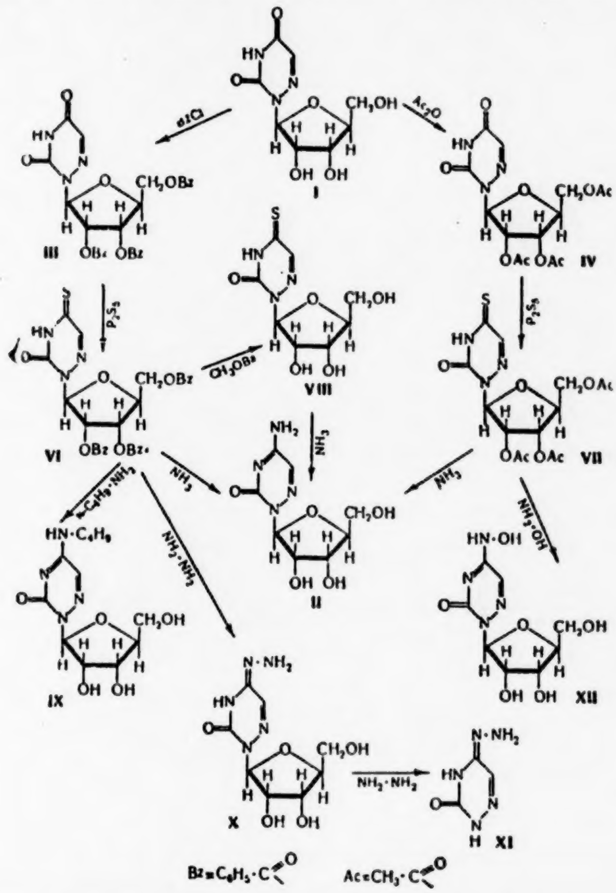
Found %: C 35.58; H 5.13; N 25.40. $C_8H_{13}O_5N_3$. Calculated %: C 35.60; H 4.88; N 27.15.

2) N'-amino-6-azacytosine (XI), as yellow needles decomposing above 240°, with R_f values 0.24 (in system B), and 0.82 (in system C).

Found %: C 28.19; H 4.17; N 54.48. $C_3H_5ON_5$. Calculated %: C 28.30; H 3.94; N 55.10.



The reaction of peracetyl-4-thio-6-azauridine with hydroxylamine gave N'-hydroxy-6-azacytidine (XII), obtained as white needles; m. p. 234-235.5°, with R_f values 0.14 (in system A), and 0.43 (in system B).

Found %: C 37.18; H 4.54; N 21.38. $C_8H_{12}O_6N_4$. Calculated %: C 36.92; H 4.64; N 21.53.

By boiling in acid medium, 6-azacytidine and its derivatives are gradually converted into 6-azauridine (I). Under analogous conditions, N'-amino-6-azacytosine gives 6-azauracil.

Preliminary experiments were carried out to investigate the influence of azacytidine on experimental tumors. Experiments were done on mice with ascite cancer and Ehrlich carcinoma. In experiments with ascite cancer, 6-azacytidine was introduced intraperitoneally in physiological solution during eight days starting on the second day after transplantation; the dose was 250 mg/kg, and the number of mice experimented with, 10. As in the case of 6-azauridine, mice treated with 6-azacytidine had a slightly longer life (by 17%) as compared with controls. In experiments with Ehrlich carcinoma, 6-azacytidine was introduced in a group of ten mice in a similar way during 9 days, starting on the fourth day after innoculation. The tumors were removed 15 days after innoculation. It was found that the mean weight of tumors was 345 mg in treated animals, against 379 in untreated animals. In another experiment, 6-azacytidine was administered in the same way together with thymine-alkylamine (9 x 250 γ/kg). The mean weight of tumors was 261 mg, showing statistically a considerable lowering (t-test). In a similar experiment with 6-azauridine and thymine-alkylamine, the weight of tumor decreased only to 314 mg. These experiments show that 6-azacytidine, in combination with thymine-alkylamine noticeably retards the growth of Ehrlich carcinoma. Like 6-azauridine, 6-azacytidine has a very low toxicity.

A more detailed communication on the study of 6-azacytidine and its derivatives will be published in the journal Collection of Czechoslov. Chem. Commun.

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1. F. Sorm, A. Jakubovic, and L. Slechta, Exper. 12, 271 (1956); F. Sorm, and H. Keilova, Exper. 14, 215 (1958); J. Skoda and F. Sorm, Coll. Czechoslov. Chem. Commun. 21, 1328 (1956); J. Skoda, J. Kara, Z. Sormova, and F. Sorm, Biochim. et biophys. acta 33, 579 (1959); J. Gut, J. Moravek, C. Parkanyi, M. Prystas, J. Skoda, and F. Sorm, Coll. Czechoslov. Chem. Commun. 24, 3154 (1959).
2. J. Skoda, V. F. Hess, and F. Sorm, Exper. 13, 150 (1957); Coll. Czechoslov. Chem. Commun. 22, 1330 (1957).
3. Biosynthesis of Nucleic Acids, G. B. Brown and P. M. Roll, The Nucleic Acids, II (E. Chargaff and J. N. Davidson, eds.), New York, 1955, p. 350.
4. J. J. Fox, D. V. Praag, I. Wempen, I. L. Doerr, L. Cheong, J. E. Knoll, M. L. Eidinoff, A. Bendich, and G. B. Brown, J. Am. Chem. Soc. 81, 178 (1959).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

Soviet Journals Available in Cover-to-Cover Translation

ABBREVIATION	RUSSIAN TITLE	TITLE OF TRANSLATION	PUBLISHER	TRANSLATION BEGAN Vol.	Issue	Year
AÉ	Atomnaya énergiya	Soviet Journal of Atomic Energy	Consultants Bureau	1	1	1956
Akust. zh.	Akusticheskii zhurnal	Soviet Physics – Acoustics	American Institute of Physics	1	1	1955
	Antibiotiki	Antibiotics	Consultants Bureau	4	1	1959
Astr(on). zh(urn).	Astronomicheskii zhurnal	Soviet Astronomy–AJ	American Institute of Physics	34	1	1957
Avto(mat). svarka	Avtomaticheskaya svarka	Automatic Welding	British Welding Research Association (London)		1	1959
	Avtomatika i Telemekhanika	Automation and Remote Control	Instrument Society of America	27	1	1956
	Biofizika	Biophysics	National Institutes of Health*		1	1957
	Biokhimiya	Biochemistry	Consultants Bureau	21	1	1956
Byull. éksp(erim). biol. i med.	Byulleten' éksperimental'noi biologii i meditsiny	Bulletin of Experimental Biology and Medicine	Consultants Bureau	41	1	1959
DAN (SSSR) Dokl(ady) AN SSSR	Doklady Akademii Nauk SSSR	The translation of this journal is published in sections, as follows:				
	Life Sciences	Doklady Biochemistry Section	American Institute of Biological Sciences	106	1	1956
	Life Sciences	Doklady Biological Sciences Sections (Includes: Anatomy, biophysics, cytology, ecology, embryology, endocrinology, evolutionary morphology, genetics, histology, hydrobiology microbiology, morphology, parasitology, physiology, zoology sections)	American Institute of Biological Sciences	112	1	1957
	Life Sciences	Doklady Botanical Sciences Sections (Includes: Botany, phytopathology, plant anatomy, plant ecology, plant embryology, plant physiology, plant morphology sections)	American Institute of Biological Sciences	112	1	1957
	Chemical Sciences	Proceedings of the Academy of Sciences of the USSR, Section: Chemical Technology	Consultants Bureau	106	1	1956
	Chemical Sciences	Proceedings of the Academy of Sciences of the USSR, Section: Chemistry	Consultants Bureau	106	1	1956
	Chemical Sciences	Proceedings of the Academy of Sciences of the USSR, Section: Physical Chemistry	Consultants Bureau	112	1	1957
	Earth Sciences	Doklady Earth Sciences Sections (Includes: Geochemistry, geology, geophysics, hydrogeology, mineralogy, paleontology, petrography, permafrost sections)	American Geological Institute	124	1	1959
	Earth Sciences	Proceedings of the Academy of Sciences of the USSR, Section: Geochemistry	Consultants Bureau	106-123	1 6	1957-1958
	Earth Sciences	Proceedings of the Academy of Sciences of the USSR, Sections: Geology	Consultants Bureau	106-123	1 6	1957-1958
	Mathematics	Doklady Soviet Mathematics	The American Mathematics Society	131	1	1961
	Physics	Soviet Physics–Doklady (Includes: Aerodynamics, astronomy, crystallography, cybernetics and control theory, electrical engineering, energetics, fluid mechanics, heat engineering, hydraulics, mathematical physics, mechanics, physics, technical physics, theory of elasticity sections)	American Institute of Physics	106	1	1956
	Physics	Proceedings of the Academy of Sciences of the USSR, Applied Physics Sections (does not include mathematical physics or physics sections)	Consultants Bureau	106-117	1	1956-1957
Derevoobrabat. prom-st'.	Derevoobrabatyvayushchaya promyshlennost'	Wood Processing Industry	Timber Development Association (London)		9	1959
	Élecktrosvyaz	Telecommunications	Massachusetts Institute of Technology*		1	1957
Éntom(ol). oboz(renie)	Éntomologicheskoe obozrenie	Entomological Review	American Institute of Biological Sciences	38	1	1959
Farmakol. (i) toksikol(ogiya)	Farmakologiya i toksikologiya	Pharmacology and Toxicology	Consultants Bureau	20	1	1957
FMM	Fizika metallov i metallovedenie	Physics of Metals and Metallography	Acta Metallurgica*	5	1	1957
Fiziol. zhurn. SSSR (im. Sechenova)	Fiziologicheskii zhurnal im. I. M. Sechenova	Sechenov Physiological Journal USSR	National Institutes of Health*		1	1957
Fiziol(ogiya) rast.	Fiziologiya rastenii	Plant Physiology	American Institute of Biological Sciences	4	1	1957
	Geokhimiya	Geochemistry	The Geochemical Society		1	1958
FTT	Fizika tverdogo tela	Soviet Physics–Solid State	American Institute of Physics	1	1	1959
Izmerit. tekh(nika)	Izmeritel'naya tekhnika	Measurement Techniques	Instrument Society of America		1	1959
Izv. AN SSSR, O(td). Kh(im). N(auk)	Izvestiya Akademii Nauk SSSR: Otdelenie khimicheskikh nauk	Bulletin of the Academy of Sciences of the USSR: Division of Chemical Sciences	Consultants Bureau		1	1952

continued

Izv. AN SSSR, O(td). T(ekhn). N(auk): Met(all). i top.	(see Met. i top.)					
Izv. AN SSSR Ser. fiz(ich).	Izvestiya Akademii Nauk SSSR: Seriya fizicheskaya	Bulletin of the Academy of Sciences of the USSR: Physical Series	Columbia Technical Translations		1	1954
Izv. AN SSSR Ser. geofiz.	Izvestiya Akademii Nauk SSSR: Seriya geofizicheskaya	Bulletin (Izvestiya) of the Academy of Sciences USSR: Geophysics Series	American Geophysical Union		1	1954
Izv. AN SSSR Ser. geol.	Izvestiya Akademii Nauk SSSR: Seriya geologicheskaya	Izvestiya of the Academy of Sciences of the USSR: Geologic Series	American Geological Institute		1	1958
Kauch. i rez.	Kauchuk i rezina	Soviet Rubber Technology	Research Association of British Rubber Manufacturers	18	1	1959
	Kinetika i kataliz	Kinetics and Catalysis	Consultants Bureau	1	3	1960
	Koks i khimiya	Coke and Chemistry USSR	Coal Tar Research Association (Leeds, England)		1	1958
Kolloidn. zh(urn).	Kolloidnyi zhurnal	Colloid Journal	Consultants Bureau	14	1	1952
	Kristallografiya	Soviet Physics – Crystallography	American Institute of Physics	2	1	1957
Metalov. i term. obrabot. metal.	Metallovedenie i termicheskaya obrabotka metallov	Metal Science and Heat Treatment of Metals	Acta Metallurgica	6	1	1958
	Metallurg	Metallurgist	Acta Metallurgica		1	1957
Met. i top.	Metallurgiya i topliva	Russian Metallurgy and Fuels	Eagle Technical Publications		1	1960
Mikrobiol.	Mikrobiologiya	Microbiology	American Institute of Biological Sciences	26	1	1957
OS	Optika i spektroskopiya	Optics and Spectroscopy	American Institute of Physics		6	1959
	Pochvovedenie	Soviet Soil Science	American Institute of Biological Sciences		1	1958
	Priborostroenie	Instrument Construction	British Scientific Instrument Research Association		1	1959
Pribory i tekhn. éks(perimenta)	Pribory i tekhnika éksperimenta	Instruments and Experimental Techniques	Instrument Society of America		1	1957
Prikl. matem. i mekh.	Prikladnaya matematika i mekhanika	Applied Mathematics and Mechanics	American Society of Mechanical Engineers		1	1958
PTÉ	(see Pribory i tekhn. éks.)					
	Problemy Severa	Problems of the North	National Research Council of Canada			
Radiotekh.	Radiotekhnika	Radio Engineering	Massachusetts Institute of Technology*	12	1	1957
Radiotekh. i élektronika	Radiotekhnika i élektronika	Radio Engineering and Electronics	Massachusetts Institute of Technology*	2	1	1957
	Stanki i instrument	Machines and Tooling	Production Engineering Research Assoc.		1	1959
	Stal'	Stal (In English)	Iron and Steel Institute		1	1959
Stek. i keram.	Steklo i keramika	Glass and Ceramics	Consultants Bureau	13	1	1956
Svaroch. proiz-vo	Svarochnoe proizvodstvo	Welding Production	British Welding Research Association		4	1959
Teor. veroyat. i prim.	Teoriya veroyatnostei i ee primenenie	Theory of Probability and Its Applications	Society for Industrial and Applied Mathematics		1	1956
Tsvet. Metally	Tsvetnye metally	Nonferrous Metals	Primary Sources		1	1960
UFN	Uspekhi fizicheskikh Nauk	Soviet Physics – Uspekhi (partial translation)	American Institute of Physics	66	1	1958
UKh	Uspekhi khimii	Russian Chemical Reviews	The Chemical Society (London)		1	1960
UMN	Uspekhi matematicheskikh nauk	Russian Mathematical Surveys	London Mathematical Society	15	1	1960
Usp. fiz. nauk	(see UFN)					
Usp. khim(ii)	(see UKh)					
Usp. matem. nauk	(see UMN)					
Usp. sovr. biol.	Uspekhi sovremennoi biologii	Russian Review of Biology	Oliver and Boyd		48	1959
Vest. mashinostroeniya	Vestnik mashinostroeniya	Russian Engineering Journal	Production Engineering Research Assoc.		4	1959
Vop. gem. i per. krovi	Voprosy gematologii i perelivaniya krovi	Problems of Hematology and Blood Transfusion	National Institutes of Health*		1	1957
Vop. onk.	Voprosy onkologii	Problems of Oncology	National Institutes of Health*		1	1957
Vop. virusol.	Voprosy virusologii	Problems of Virology	National Institutes of Health*		1	1957
Zav(odsk). lab(oratoriya)	Zavodskaya laboratoriya	Industrial Laboratory	Instrument Society of America	25	1	1959
ZhAKh Zh. anal(it). khimii	Zhurnal analiticheskoi khimii	Journal of Analytical Chemistry USSR	Consultants Bureau	7	1	1952
ZhETF / Zh. éksperim. i teor. fiz.	Zhurnal éksperimental'noi i theoreticheskoi fiziki	Soviet Physics—JETP	American Institute of Physics	28	1	1955
ZhFKh Zh. fiz. khimii	Zhurnal fizicheskoi khimii	Russian Journal of Physical Chemistry	The Chemical Society (London)		7	1959
ZhMÉI Zh(urn). mikrobiol. épidemiol. i immunobiol.	Zhurnal mikrobiologii, épidemiologii i immunobiologii	Journal of Microbiology, Epidemiology and Immunobiology	National Institutes of Health*		1	1957
ZhNKh / Zh(urn). neorgan(ich). khim(ii)	Zhurnal neorganicheskoi khimii	The Russian Journal of Inorganic Chemistry	The Chemical Society (London)		1	1959
ZhOKh / Zh(urn). obshch(ei) khimii	Zhurnal obshchei khimii	Journal of General Chemistry USSR	Consultants Bureau	19	1	1949
ZhPKh / Zh(urn). prikl. khimii	Zhurnal prikladnoi khimli	Journal of Applied Chemistry USSR	Consultants Bureau	23	1	1950
ZhSKh / Zh(urn). strukt. khimii	Zhurnal strukturnoi khimii	Journal of Structural Chemistry	Consultants Bureau	1	1	1960
ZhTF / Zh(urn). tekhn. fiz.	Zhurnal teknicheskoi fiziki	Soviet Physics—Technical Physics	American Institute of Physics	26	1	1956
Zh(urn). vyssh. nervn. deyat. (im. Pavlova)	Zhurnal vysshei nervnoi deyatel'nosti (im. I. P. Pavlova)	Pavlov Journal of Higher Nervous Activity	National Institutes of Health*		1	1958

*Sponsoring organization. Translation through 1960 issues is a publication of Pergamon Press.

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.—Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. — Publisher.